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ELEMENTS OF CHEMISTRY

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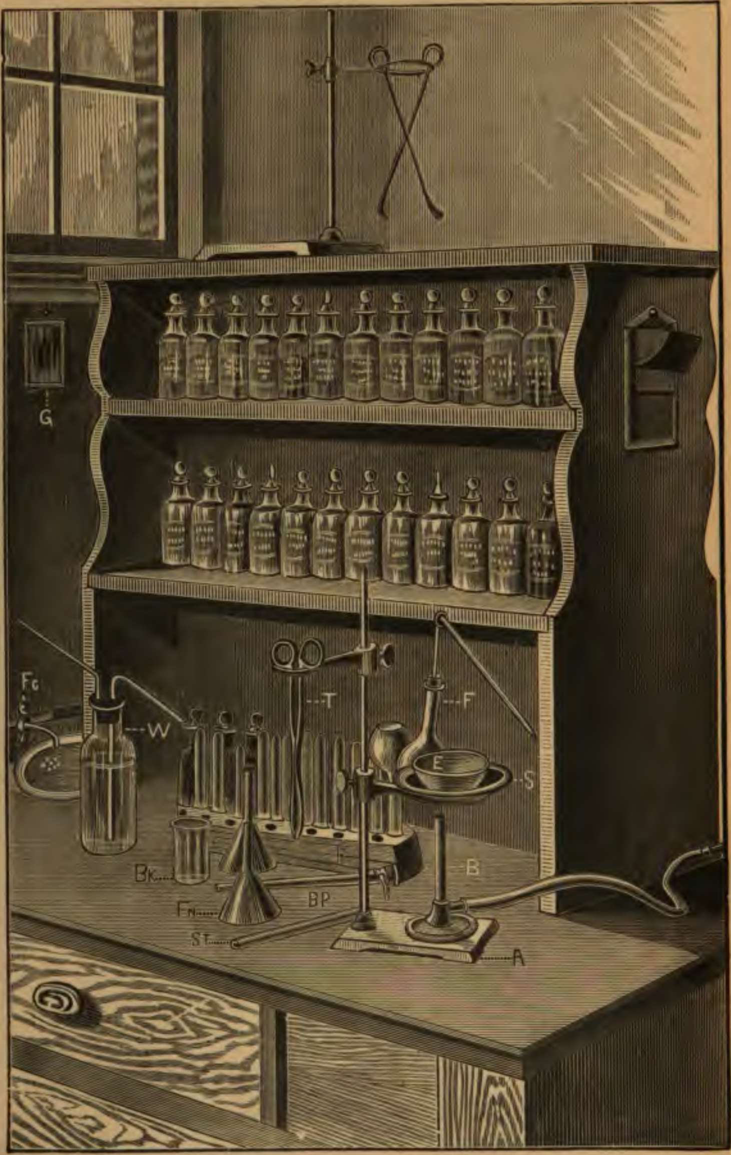
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ELEMENTS

OF

INORGANIC CHEMISTRY,

DESCRIPTIVE AND QUALITATIVE.

BY

JAMES H. SHEPARD,

PROFESSOR OF CHEMISTRY, SOUTH DAKOTA AGRICULTURAL COLLEGE,
AND CHEMIST FOR THE EXPERIMENT STATION.

BOSTON, U.S.A.,
D. C. HEATH & CO., PUBLISHERS.
1891.

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FROM

Julius R. Wakefield

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TO THE TEACHER.

I.

METHODS.

It is with no little diffidence that the author approaches the subject of Methods. He is fully aware that every teacher has his own method, and that all successful methods are entitled to respectful consideration. There are, however, some principles upon which all are agreed, and a classification and a brief discussion of the different methods which have been employed may at least prove suggestive.

The problems before us are these: —

1. If we teach chemistry at all, what advantages has this science to offer as factors in developing the youthful mind, and what good results will follow its study?

2. If the study of chemistry be positively desirable, what method of presentation will best accomplish the desired results?

1. Neglecting for the present the claims of those who would become chemists by profession, let us consider chemistry as a means of education. In this capacity, when properly taught, chemistry awakens and cultivates a spirit of investigation; it encourages the student to ask Nature questions, and it is unexcelled by any other branch of learning in the clearness and conclusiveness of the answers received; it insists upon the strictest habits of observation; it leads to the concentration of thought and of energy; it educates the senses; it trains the hand to delicate manipulation; it exercises the faculty of reason and the power of judging; it affords useful information peculiarly

its own, and thus forms an important part of a good, general education.

Backed by such advantages as these, it really seems that chemistry should be deemed worthy of a place in all liberal as well as in purely scientific education.

2. When it comes to methods of instruction, the teacher has many from which to choose. These methods may be arranged approximately under four general divisions: —

(1) The Classical or Didactic method.

(2) The Laboratory method, in which the teacher does all the experimentation in the presence of the class, and accompanies the experimentation by didactic instruction.

(3) The Working-Laboratory method, in which the student does his own experimentation, and receives little or no didactic instruction. This method varies somewhat, in its application: —

(*a*) The student may be required to work with no aid from text-books, etc., relying upon his work alone for the benefits to be obtained, the instructor in this case acting really as a demonstrator.

(*b*) The student may have a text-book as a guide, the instructor acting as before.

(4) A method which the author begs leave to christen THE SCIENTIFIC METHOD; this embodies all the good features of the preceding methods.

The experience of many careful instructors would warrant the following estimate of the relative value of these methods: —

The first method affords some special information; otherwise, chemistry, when thus taught, is equalled as an educational factor, by history, and by kindred subjects; and is excelled by mathematics and the classics.

The second method accomplishes as much as the first, and to a very limited extent cultivates observation; farther than this, no advantages are to be gained by its use.

The third method incites to investigation; trains the senses to observe; trains the hand to careful manipulation; and encourages the student to originate. But (*a*) is too slow; it requires more time than can be devoted to this study; and although the student may "know well what little he does know," his reasoning powers are not developed, and his fund of information is not sufficiently increased. (*b*) accomplishes its ends somewhat more rapidly than (*a*), and consequently yields more information in a given length of time; otherwise, it is not better than (*a*). As a rule, students taught by the third method are very weak in chemical theory.

An insight into the fourth method may best be obtained by a description of the manner of its application. This method contemplates: didactic instruction by the teacher; a good text-book, and as many books of reference as possible; much work by the student, who should keep a careful record of all work done, and who should recite frequently; and work by the teacher, either in the presence of the class where the class is large, or personal directions to the student when the class is small.

The use of this method is extremely simple. The teacher assigns a lesson from the text, indicating such parallel reading as the time at the student's disposal may permit; he then goes over the lesson, and gives such working directions and cautions as the subject and the student's capabilities may demand, thus, in most cases at least, saving the student from wasting his time in repeating the useless blunders of those who worked centuries ago; if the experiments be dangerous, or if the line of work be new, the teacher either makes the experiment for the class with little or no explanation, or he explains the general principles, leaving the student, when safety permits, to work out the details; after this, the student is sent to his desk, where he works, reads, and makes his notes for the next recitation.

The following day the student is questioned concerning his work, and is encouraged to tell truthfully and exactly how he succeeded, if he has succeeded, or why he failed, if he has failed.

In case the student has failed, and does not know the reason, or gives the wrong reason, the teacher, meanwhile explaining nothing himself, calls upon other members of the class until the point in question is elucidated. If all have failed, which rarely happens, the teacher gives directions anew, and the students try again. In general, the teacher aims to do as little work for the class as possible, and to tell the student nothing that he can find out for himself in a reasonable length of time.

Reviews and those topics which are necessary to the science as a whole, and which are not covered by the student's work, are faithfully taught by didactic methods.

Variety is introduced and practical results are obtained in several ways, and thus the student's interest is never permitted to flag. Students are assigned essays upon various topics; are given unknown substances to analyze; are required to make analyses of substances with which they are familiar, such as coins, worn-out articles of jewelry, alloys, common salt, baking-powder, samples of drinking-water, crude drugs from the drug store, etc., etc.

In keeping his notes, the student constantly recognizes the fact that the knowledge he is seeking is to be drawn from phenomena observed while working with known factors. A good form for the headings of a note-book is as follows: —

1. Required Conditions.
2. Known Conditions.
3. Operations.
4. Conclusions.

Under 1 the student enumerates what he wishes to know; under 2 he enumerates his working materials; under 3 he tells what he does; and under 4 what conclusions he has reached.

In making his notes, the student is warned that he may err: (1) by taking a trivial required condition; (2) by assuming a required condition that will not follow from the premises; (3) by an indefinite or obscure description of his operations; (4) by reaching a conclusion more general than the premises warrant; and (5) by employing bad English in any of the preceding divisions.

In this book, written with special reference to the fourth method, the student's work, so far as practicable, is not forestalled by telling him what phenomena are to occur, and many queries are left to be answered by an experiment which the student may devise. In the closing portions of the book, all experiments (as such) are purposely omitted with the suggestion that, as the student is no longer, in the strict sense of the word, a beginner, he should be thrown still farther upon his own resources. He is asked to prepare various salts and compounds of the metals, and to describe their preparation as experiments; this is work well adapted to afford an exercise more exacting than anything previously attempted. Another good exercise for the student is to prepare working solutions for himself and his classmates, starting with the crude materials.

By this method, the student will not only secure a lasting benefit from chemistry, as an educator of hand and mind, but in case he so desires, he will find himself amply prepared for further pursuing this delightful study.

II.

WHAT SHOULD THE STUDENT MEMORIZE?

As in all other studies, this question is frequently asked concerning chemistry. In the curriculum of all schools in which chemistry is taught to beginners other studies are found, or should be found, which are peculiarly adapted to cultivate the faculty of memory; the amount of memorizing required in chemistry should be quite limited, depending more or less upon the curriculum itself.

In general, it is safe to say that much valuable time has been frittered away by requiring the student to memorize unimportant details which not even an expert retains. Because certain facts or numerical data are given in a text, it does not follow that the student's memory must be burdened with them; there are other uses for such data, and especially so in a working text. Thus, for example, the weight of one litre of a gas, atomic heats, specific gravities, densities, etc., etc., may be utilized in solving problems.

It is not even necessary to memorize the atomic weights or such units as the weight of one litre of hydrogen, since the student will learn these data by frequently using them, just as we all have learned the multiplication table. It is, however, a positive advantage to have these data given in the body of the text, since a frequent reference to them serves in a certain way as a review.

Again, the author has never required his classes to memorize tests and separations, and still his students, by way of final work, have been able correctly to analyze complex unknown solutions without the aid of reference books or of text-books; this was accomplished by simply giving the student much work to do, and then *by asking him to explain his work.* And again, it would be manifestly absurd to require the student to memorize the language of the text in experiments. And finally it should suffice to bear in mind that to be able *to do*, *to reason*, *to originate*, is far better than to be able to repeat from memory things not half understood.

III.

A BRIEFER COURSE.

FOR various reasons some teachers may wish to use certain portions of the text and to omit the rest. There is no reason why this may not be done. Experience has shown that, in a working text, even of the most elementary character, it is desirable to have the book quite complete, thus lightening the labor of the teacher, and providing for emergencies which often and unexpectedly arise. For example, one piece of apparatus may be broken, or it may be wanting, while another, which may be made to answer the same purpose, is available; or, a student in his work may come upon something which not even the teacher could foresee; one chemical may have been entirely consumed, while another, which will answer, may still be plentiful, etc., etc. In view of all these considerations, it is evident that a somewhat full text will be more satisfactory to both student and teacher, even though certain portions of it are omitted, or dwelt upon quite lightly. There is no truth in the tradition that "to omit certain parts of a book causes the student to be less thorough"; on the contrary, such a process should teach him to select what he really wants from what he does not want, — a lesson he must learn sooner or later. There is one thing, at least, that a full text certainly does do, and that is, it forever banishes from the student's mind the idea that he has learned all there is to know of chemistry.

The following hints may serve to show how the work may be lessened or how the course may be shortened: —

1. Omit the experiments marked OP.

2. When two or more experiments tend toward the same general result, omit as many as desirable, selecting those most readily performed by the apparatus and working material available.

3. Omit the rarer elements and their compounds.

4. In the compounds of the common elements, dwell at length upon the most useful ones, *e.g.*, in the compounds of nitrogen, place the stronger work upon ammonia, nitrogen monoxide, and nitric acid, omitting or dwelling but briefly upon the remaining compounds.

5. The qualitative work may be curtailed by omitting some of the separations, etc.

6. Sometimes, also, the teacher may prefer to modify the order of presenting the various topics; for example, he may wish to discuss molecules more thoroughly at the outset, or he

may wish the class to experiment with the oxides of nitrogen before discussing them in their bearing upon the law of multiple proportions, etc., etc. In this way he may conform to his own ideas of presentation.

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HISTORICAL SKETCH.

1. The word **Chemistry** is probably derived from *Chemia*, which is an old name for Egypt. The word signifies simply the Egyptian art; and it was so called since chemistry was first practised by the Egyptians.

Like all sciences which have to deal with Nature, chemistry has been developed by a long and tedious series of experiments. Since the art of experimenting is a comparatively modern one, the **Ancients,** as one would naturally infer, were not deeply versed in this science. The principal obstacle in the way of their progress is apparent when we know that they made great use of the speculative method; that is, when they wanted an explanation of any fact in Nature, they simply thought about it, without seeking to verify their conclusions by the test of rigid experiment.

The Egyptian priests were the learned class of their time; and their researches were carried on with such an air of mystery, and at such uncanny times, and in such secret places, that Chemistry was spoken of as the Black, or Secret Art. We find, however, that the Egyptians possessed a considerable knowledge of the arts of dyeing, painting, and glass-making; and that they were quite skilled in metallurgy and the manufacture of pottery.

About the time of Aristotle (fourth century B.C.) it was believed by some that all bodies are only modifications of one fundamental substance; by others, that all substances are but the dwelling-places of four properties, — viz., heat, cold, moisture, and dryness, — and that these four properties of matter are best represented in the four substances, fire, air, water, and earth. It was further believed that these properties could be transferred from one body to another, and, as a consequence, that the ordinary metals, such as iron, could be transformed into the noble metal, gold. It will be readily understood that this thought furnished a powerful incentive to work, which incidentally contributed something towards the advancement of chemistry. Considering the object he had in view, it is not surprising that the chemist practised his art in caverns and at night, where no prying eyes could see his operations, nor that he recorded his transactions in ambiguous terms and in mysterious characters.

We thus find the ancients making but little progress in true chemical science. Moreover, we now know that their pernicious methods and theories were detrimental for many centuries afterwards, notwithstanding the fact that chemistry originated in these self-same theories and methods.

2. The **Arabs**, in the year 640 A.D., invaded Egypt and became acquainted with the Egyptian sciences.

Geber, an Arabian alchemist of the eighth century (the Arabs gave chemistry the name *Al-Chemia*), wrote the first book on chemistry. He understood many chemical manipulations, discovered a solvent for gold, a mixture of nitric and hydrochloric acids or *aqua regia*, and proposed the first theory of the chemical composition of the metals, viz., that sulphur and mercury were the simple or primary substances from which all the different metals are derived.

In this period, then, we find an encouraging advance; chemical processes are becoming more generally known, and a suggestive though erroneous theory is announced, which is destined to develop, through many modifications, from error into truth. As an instance of the manner in which this theory was afterwards modified and extended, we may here mention the fact that Basil Valentine of the fourteenth century, accepting sulphur and mercury as the primal elements, extended the conception to all substances; and that Boyle, three centuries later, doubtlessly influenced by this same theory to investigate this problem, announced the true solution.

3. During the **Middle Ages** the Arabians fostered the sciences. Their academies in Spain were sought by students from all parts of the civilized world; these philosophers, returning to their native countries, taught chemistry there. Thus we find, in the thirteenth century, Raymond Lully in Spain, Albertus Magnus in Germany, Arnold Villanovanus in France, and Roger Bacon in England. All these believed in the transmutation of the metals, and the philosophy of their time teemed with mysticism and nonsense. We must here note that the all-absorbing theme was the Philosopher's Stone, a substance which should transform the baser metals into precious gold. The writings of this period are extravagant, confused, and purposely so written that they are nearly unintelligible. Bacon, however, to clear himself of the charge of sorcery (chemistry was still the Black Art), wrote a treatise in which he showed that many things supposed to be caused by supernatural agencies are produced by natural causes.

The search for the Philosopher's Stone during this period brought to light many facts in inorganic chemistry; and thus do we find alchemy slowly but surely paving the way for genuine chemistry.

4. In the era of **Medical Chemistry,** chemists directed their investigations into a different channel. They then sought the *Elixir Vitae*, or Elixir of Life, — a cordial which should cure all the ills of mankind, and give perpetual youth. By a strange misinterpretation of Aristotle, some chemists also conceived the idea that the Philosopher's Stone, when found, would achieve the same results.

Paracelsus (1493–1541) was the most noted of these investigators. By his great achievements he earned the title, The Father of Medicine.

Agricola (1490–1555) wrote the first treatise on Metallurgy and Mining.

Libavius wrote the first Hand-Book of Chemistry, his *Alchemia*, which was published in 1595.

Van Helmont (1577–1644) deserves special mention, since he was the first to emancipate himself from the theories of the Aristotelian school. He also discovered various gases, and showed that metals are not destroyed when dissolved in acids. But he, too, had his delusion: it was his *Alkahest*, a universal solvent as well as a universal medicine.

Robert Boyle (1627–1691) advanced still further: he claimed that the exact number of the elements was not known, and he clearly stated the difference between the elements and the compound substances. He also raised chemistry to the dignity of a true science, which was not to be studied as a part of any other, but as one of the great Natural Sciences.

During this period many useful and potent medicines were discovered, and, although error was by no means completely banished, the fundamental principles of chemistry were well grounded in truth. Hereafter, the history of chemistry is a history of improvements, discoveries, and researches extending to all the different branches into which this science has developed.

5. **Pneumatic Chemistry** was the next phase in the development of our science. This period was remarkable for the investigation of the properties of gases, and the phenomena of combustion.

Stahl sought to explain combustion by assuming the existence of a combustible principle, or element, which he termed *Phlogiston.* According to his views, this element must be *taken away* from combustible bodies to render them incombustible.

Among the believers in Phlogiston were three remarkable men: —

1. Joseph Priestley, who discovered oxygen gas in 1774, and afterwards other and important gases.
2. Henry Cavendish (1731–1810), who experimented with inflammable air (hydrogen gas), determined the *density* of the gases, and discovered the unvarying composition of the atmosphere.
3. Charles William Scheele (1742–1786), a Swedish chemist, who discovered chlorine gas, prussic acid, glycerine, and the pigment, Scheele's green. He also made such other researches that he is entitled to be placed among the founders of *Quantitative Analysis.*

None of these three ever discovered the true explanation of combustion. The Phlogiston theory, however, could not stand the test of rigid experiment; and Lavoisier, by exposing its fallacies, ushered in the new era of chemistry, or

6. The Modern Era. — From his own experiments and those of his predecessors, Lavoisier determined that a burning body unites with, or *takes up* a combustible element, oxygen. By the use of the balance he discovered the great fundamental truth, that, however great the changes matter may undergo, no loss in weight occurs, or, in other words, that matter is indestructible. He also introduced a system of chemical nomenclature, which has been of inestimable value, as chemists not only disagreed as to the names of the substances with which they were acquainted, but often and purposely called one substance by so many names that their meaning was not at all certain.

Dalton, next to Lavoisier, gave a great impetus to the study of chemical phenomena by the discovery of the laws of *combination*, known as the laws of "definite and multiple proportions," and by the propounding of the *atomic theory.*

Gay Lussac discovered the law of combination of gases by *volume.*

In 1808 Sir Humphry Davy discovered, by means of electrolysis, the compound nature of the alkalies.

In 1828 Wöhler prepared urea from inorganic substances, thus crossing out the division line between organic and mineral chemistry.

Spectrum analysis, dating back scarcely farther than 1860, has not only revealed the existence of many new terrestrial elements, — such as caesium, thallium, rubidium, indium, etc., — but has enabled us to determine the composition of the sun and stars themselves.

Chemistry is no longer the Black Art, nor the handmaid of astrology, but a legitimate science, exact in its methods, and beneficent in its results. While, as a pure science, its aim is the investigation of truth, it has in its practical application formed an important factor in the industries of all civilized countries.

SUGGESTION. Read Rodwell's *Birth of Chemistry;* Roscoe's *Spectrum Analysis;* Whewell's *History of the Inductive Sciences*, pp. 261–310; Roscoe and Schorlemmer's Treatise, pp. 1–40. Write short biographical sketches of the chemists mentioned (consult an Encyclopedia).

INTRODUCTION.

DEFINITIONS.—LAWS OF COMBINATION IN DEFINITE AND MULTIPLE PROPORTIONS.—ATOMIC THEORY.—ATOMIC WEIGHTS.—NAMES OF ELEMENTS.—SYMBOLS.—TABLE OF THE ELEMENTS.

7. **To Experiment** with a substance is to place it under certain conditions or with certain substances to ascertain its properties and behavior.

An experiment is a question intelligently put to Nature.

EXPERIMENT 1 P. (To the student.) Since this is your first experiment in chemistry, you may feel uncertain as to what you are expected to do, or how you are to derive the most benefit from your work. In general, it is a safe policy always to work carefully, and to note all phenomena that occur; from these phenomena you are then expected to derive certain desired conclusions. It is true, that, for various reasons, you may sometimes need assistance in reaching these conclusions; in such cases you must necessarily rely upon the experience of others. Although this latter method is a legitimate and often an indispensable way of obtaining knowledge, we may safely say that he has the most truly scientific spirit and methods, who, so far as possible, works and observes for himself.

In the experiments you are about to make, you may watch for any *changes* that take place in the substances experimented upon. Some of these changes may be perceptible to the sense of sight, and some to the sense of smell; others may be perceptible to the sense of touch; and still others to general sensibility; but, as a usual thing, the chemist depends mainly upon sight and smell to detect any changes in the substances upon which he is working. Now let us ask of Nature a few questions.

Steadily and persistently hold a platinum wire in a Bunsen flame (Art. 28). What occurs? Now cut off a very short piece (say 2^{mm}) of the wire, place it upon a piece of charcoal, and heat it by means of the blow-pipe flame (Art. 28). What takes place? Then cover the bit of wire with a mixture of sodium carbonate (Na_2CO_3) and potassium nitrate (KNO_3), and slightly moisten the whole. Again heat in the blow-pipe flame as before. What results? Now wash the piece of wire clean, and place it in a test-tube; then add nitric acid (HNO_3), and warm gently in the Bunsen flame. What occurs? Again wash the wire, add hydrochloric acid (HCl), and warm as before. What have you observed? You may possibly be inclined to answer, "Nothing of importance." But let us see. *Did you succeed in separating the platinum into two or more different substances?* Assuredly not; nor could you have so separated it by any process known to man. Now that is important, since there are, besides platinum, about sixty-eight other substances that have not been separated into simpler ones: and these should have a class name. Hence the following name and definition: —

8. **An Element** is a substance that has not been divided into two or more simpler substances.

EXAMPLES. Gold, Iron, Silver, Tin, Oxygen, Potassium.

NOTE (to the student). You are not to infer that all these sixty-eight elements would behave precisely like platinum: such, indeed, is not the case. Very few of them could have withstood the above treatment without undergoing marked changes. None of them, however, would have yielded two different substances, in which respect alone do they all agree with platinum.

QUERY. What is a definition?

SUGGESTION. Try, as above, bits of lead, copper, iron, zinc, etc. Compare the results with those obtained from platinum.

EXP. 2 P. Place in a test-tube a short piece of thoroughly dried pine wood as thick as a lead-pencil. Heat it over a Bunsen flame, or a spirit-lamp. What collects on the sides of the tube, what escapes, and what remains behind? Burn this remainder on platinum foil, and what will then remain?

QUERIES. What did you obtain from the wood? What became of the charcoal when burned? Did any tar escape with the smoke? How do you know? Any water? Prove it. (SUG. Hold a piece of cold glass in the escaping vapors.) Will a piece of brick give the same results? Try it.

EXP. 3 P. Place in a hard glass tube, open at both ends, a small piece of galena (PbS). Hold the tube somewhat slanting in the Bunsen flame, so that the greatest heat shall strike underneath the galena. Notice the odor of the fumes which soon issue from the tube. These are the fumes of burning sulphur. Now place the residue in a shallow, cup-shaped cavity, which you are to make in a piece of charcoal. Cover the residue with sodium carbonate (Na_2CO_3), and slightly moisten the whole. Heat it before the blow-pipe flame and you will obtain a metallic bead. What metal is it?

It is evident that wood and galena are not elements; and, as the student's experience increases, he will learn that there is a very large class of substances which can thus be separated into simpler ones, and that these simpler substances are united in definite proportions by weight. Hence the following name and definition: —

9. A Compound (chemical) consists of two or more elements chemically combined in definite proportions. (Art. 17.)

EX. Salt (NaCl); Water (H_2O); Sugar ($C_{12}H_{22}O_{11}$).

Exp. 4 p. Mix thoroughly 0.56^g of very fine iron-filings and 0.32^g powdered sulphur. Although the mixture resembles neither iron nor sulphur, this is only a mechanical mixture, and the microscope reveals the particles of iron and sulphur lying side by side: moreover, they may be separated by mechanical means. Now heat one-half the mixture to redness in an iron spoon; a glow diffuses itself throughout the mass, and the iron combines with the sulphur in definite proportions. No microscope can now distinguish the iron and sulphur particles, nor can they be separated except by chemical means. The iron and sulphur have exactly entered into chemical union.

Queries. Can you, with a magnet, separate the iron from the sulphur before heating? Try it. Will bisulphide of carbon (CS_2) dissolve out the sulphur from the iron particles before heating? Try it. Should the sulphur dissolve, evaporate the solution to dryness on a watch crystal, and see if the sulphur will remain as a residue.

After heating, pulverize the mass and try as above. What difference do you find?

From the above we derive the two following definitions: —

10. A **Mechanical Mixture** is formed when substances are put together in no definite proportions, and the resulting substance retains the properties of its constituents.

11. A **Chemical Combination** or **Reaction** takes place when two or more substances unite in definite proportions to form one or more substances entirely different from the original ones.

12. **Chemistry** is that science which treats of the *elements* found in nature, their properties, compounds, and actions and reactions upon one another.

Matter exists in three forms; viz., Solids, Liquids, and Gases.

13. **Solids** do not readily change their forms, since in them the attractive (inter-molecular) forces exceed the repellent forces.

14. **Liquids** do readily change their forms, since their attractive and repellent (inter-molecular) forces are equal, or nearly so.

15. In **Gases**, the repellent forces are greater than the attractive forces, consequently gases always tend to occupy a larger space.

SUG. Name several solids. Liquids. Gases. Show, by heating a piece of ice till it vaporizes, that water exists in all three conditions.

16. **Chemism** is an attractive force which is exerted between the elements, causing them to enter into combination with one another.

NOTE. *Cohesion* and *chemism* tend to draw particles together. In all solid and liquid compound bodies, both chemism and cohesion operate: the former holds the elements together, and determines the composition of the body; the latter holds the particles of the compound together, and gives us the mass. *Heat* is a repellent force, and tends to separate the small particles of all bodies, as is shown by the expansion of bodies when heated.

17. **Law of Definite Proportions.**—If we examine any chemical compound,—such, for example, as water, which consists of the elements hydrogen and oxygen; common salt, which consists of the elements sodium and chlorine,—we find that the compound always contains exactly the same proportions of its constituents. Water always contains 88.89 per cent of oxygen and 11.11 per cent of hydrogen; common salt always contains 39.32 per cent of sodium and 60.68 per cent of chlorine. As a result of the careful analysis of a very large number of

chemical compounds, the *law of definite proportions* was propounded. The law may be stated in this form: —

Any given chemical compound always contains the same elements in the same proportions by weight.

REM. It is, of course, impossible for the beginner to prove the correctness of this law, for the reason that the proof cannot be furnished without the employment of some of the most delicate and difficult chemical processes.

18. Law of Multiple Proportions. — Some elements form more than one compound with each other. Thus hydrogen and oxygen form not only water but hydrogen dioxide; iron and sulphur form three compounds; nitrogen and oxygen form five compounds. If we examine the proportions by weight in which the elements unite, we find very curious and interesting relations. Thus, in water we find: hydrogen 1 part, oxygen 8 parts; in hydrogen dioxide, hydrogen 1 part, oxygen 16 parts. (See Art. 38.)

In the compounds of iron and sulphur (Art. 293), there are:

Compound 1, 32 parts of sulphur and 56 parts of iron.
Compound 2, 64 " " " 56 " "
Compound 3, 96 " " " 112 " "

In the compounds of nitrogen and oxygen (Art. 56), there are:

Compound 1, 28 parts of nitrogen and 16 parts of oxygen.
Compound 2, 28 " " " 32 " "
Compound 3, 28 " " " 48 " "
Compound 4, 28 " " " 64 " "
Compound 5, 28 " " " 80 " "

The amount of oxygen in the second compound of hydrogen and oxygen is just *twice* as great, — not one and one-half, nor any fractional number of times, as great, as in the first.

The amounts of sulphur in the three compounds of iron and sulphur bear to each other the relation of 1:2:3; and the amounts of iron are to each other as 1:1:2.

Finally, in the compounds of oxygen and nitrogen, the amounts of oxygen are to each other as 1:2:3:4:5; the amount of nitrogen remaining constant.

These cases illustrate what is known as the *law of multiple proportions*, which may be stated thus:

If two elements, A and B, form several compounds with each other, and we consider any fixed amount of A, then the different amounts of B which combine with this fixed amount of A bear a simple ratio to each other.

19. Combining Number. — For each element we can select a certain number which will enable us always to express the proportion by weight in which this element enters into combination.

Thus, we may select the number 16 for oxygen, and we find that no matter what the compound may be in which we find the oxygen, its proportion may be expressed by 16 or some simple multiple of 16. In the same way we find that 32 may be selected for sulphur; 14 for nitrogen; 56 for iron, etc., etc. The figures thus selected are known as the *combining numbers*. Elements always combine with each other in the proportions expressed by their combining numbers, or by simple multiples of these numbers. Thus, according to this, if sulphur and oxygen unite, we would expect to find them in their compounds in the proportions of 32 parts of sulphur to 16 parts of oxygen; 32 parts of sulphur to 32 parts of oxygen; 32 parts of sulphur to 48 parts of oxygen, etc. Compounds corresponding to the last two proportions are known. (See Art. 164.)

20. Atomic Theory. — To account for the fact that elements unite in fixed proportions, it is assumed that all matter is made up of indivisible particles called *atoms*, and that each different kind of atom has its own particular weight. When chemical combination takes place, it is supposed that this consists of a union of the atoms of the elements which take part in the action. Thus, when iron and sulphur are brought together, at first no action takes place; but when they are very intimately mixed, and the mixture heated, it is believed that each atom of iron seizes upon an atom of sulphur, uniting with it. Now, as these atoms have definite weights, it follows that, no matter how many unite, the compound formed must always contain the elements in the proportion of the weights of the atoms.

The simplest kind of combination is that in which the elements unite in the proportion of one atom of one element to one of the other. But the elements may unite in the proportion of *one* atom of one to *two*, or *three*, or even *four* of the other, etc. Or, two atoms of one may unite with *three* of another, etc. Hence, it follows that the amounts of any element found in different compounds must bear simple relations to each other.

21. Atomic Weights. — The numbers called *combining numbers* are believed to express the *relative weights of the atoms* of the elements, and are now called *atomic weights.* The numbers now in use are intended to express the weights of the atoms of the elements as compared with the weight of the atom of hydrogen taken as unity. Thus, when we say that the atomic weight of oxygen is 16, and that of nitrogen 14, we mean that the weight of the atom of oxygen is 16 times as great as that of the atom of hydrogen; and that the weight of the atom of nitrogen is 14 times as great as that of hydrogen.

22. Determination of Atomic Weights. — To determine the atomic weight of an element is by no means a simple matter; indeed, it is extremely difficult. If all the elements united with each other in only one proportion it would not be difficult to agree upon atomic weights. Thus chlorine and hydrogen unite with each other in the proportion of 35.5 parts of chlorine to 1 of hydrogen; bromine and hydrogen in the proportion of 80 parts of bromine to 1 of hydrogen; iodine and hydrogen in the proportion of 127 parts of iodine to 1 of hydrogen; and these elements do not unite with hydrogen in any other proportions. Hence, we may assume that in the compounds formed we have, in the first place, one atom of chlorine united with one atom of hydrogen; in the second, one atom of bromine with one of hydrogen; and in the third, one of iodine with one of hydrogen. We are thus led to the conclusion that the atom of chlorine weighs 35.5 times as much as the atom of hydrogen, or that the atomic weight of chlorine is 35.5; and, in the same way, that the atomic weight of bromine is 80, and that of iodine 127.

When, however, two elements unite in more than one proportion, — and this is the rule rather than the exception, — it is clear that we must be left in doubt as to the number to select as the atomic weight. Thus, hydrogen and oxygen, as was remarked above, unite in two different proportions. In the first there are 8 parts of oxygen to 1 of hydrogen; in the second, 16 parts of oxygen to 1 of hydrogen. From this we might conclude that 8 is the atomic weight of oxygen. But we may just as well express the proportions by saying that in the first there are 16 parts of oxygen to 2 of hydrogen; and in the second, 16 parts of oxygen to 1 of hydrogen. And we might, with equal justice, conclude that 16 is the atomic weight of oxygen.

We shall find that two methods are in general use for the determination of atomic weights. The first is based upon a consideration of the specific gravity of elements and compounds in the form of gas or vapor; the second, upon the specific heat of elements and compounds. These methods will be described after some of the elements and their compounds have been considered. (Art. 157.)

23. Names of the Elements. — The ancients were acquainted with only seven elements; viz., gold, silver, copper, iron, mercury, lead, and tin. They dedicated these to the heavenly bodies; *e.g.*, silver was dedicated to the moon or *luna*. In this fanciful way some of the names of chemical compounds originated; *e.g.*, nitrate of silver is yet called *lunar caustic*.

The elements have received their names in different ways: —

1. Some retain their ancient names.
2. Some are named from some marked characteristic; *e.g.*, phosphorus, *light-bearer;* bromine, *a stench.*
3. The names of some end in "ine" or "on," to indicate a similarity of properties in those so terminating.
4. Some are named from the place of their discovery.
5. The names of recently discovered substances possessing metallic properties end in "um" or "ium."

Sug. Student find illustrations to above from Art. 25.

24. Symbols. — In expressing the composition of chemical compounds, it is desirable to have a system of symbols.

Those now in use consist of letters which stand for the names of the different elements. Thus, O stands for Oxygen, H for Hydrogen, N for Nitrogen, etc.

When only one element is known, whose name begins with a certain letter of the alphabet, that letter is used as the symbol.

When two or more are known, the names of which begin with the same letter, that one best known or first discovered is generally designated by the letter, while the others are designated by this letter and some other letter occurring in the name, *e.g.*, Carbon, C; Chlorine, Cl; Calcium, Ca; Caesium, Cs; Cadmium, Cd; Cobalt, Co; etc.

Some elements have symbols derived from their Latin names. This is perplexing to the student, but this list will explain: —

Antimony,	Sb,	from	Stibium.
Copper,	Cu,	"	Cuprum.
Gold,	Au,	"	Aurum.
Iron,	Fe,	"	Ferrum.
Lead,	Pb,	"	Plumbum.
Mercury,	Hg,	"	Hydrargyrum.
Potassium,	K,	from	Kalium.
Silver,	Ag,	"	Argentum.
Sodium,	Na,	"	Natrium.
Tin,	Sn,	"	Stannum.
Tungsten,	W,	"	Wolframium.

The symbol stands not only for the name of the element, but for its atom. Thus, O means not only oxygen, but an atom of oxygen; 2 O or O_2 means two atoms of oxygen, etc. In expressing the composition of bodies by means of these symbols, we simply place the latter side by side. Thus, HCl stands for a body which consists of hydrogen and chlorine in the proportions, 1 part by weight of hydrogen to 35.5 of chlorine; or, in terms of the Atomic Theory, it stands for a body which is formed by the union of hydrogen and chlorine in the proportion of 1 atom of hydrogen to 1 of chlorine. An expression like HCl is called *a formula.*

In expressing the composition of a body in which more than one atom of the same kind is present, a small figure is added below the line to the right of its symbol. Thus, potassium nitrate, which consists of potassium, nitrogen, and oxygen, in the proportion of 1 atom potassium, 1 nitrogen, and 3 oxygen, is written KNO_3. A large figure placed before a formula affects every symbol in the formula. Thus, if we want to express two parts of potassium nitrate, we usually write $2\ KNO_3$, and not $(KNO_3)_2$. We repeat a group of atoms (NO_3, NH_4, etc.) which we wish to keep together as a whole (Art. 159), thus: $Pb(NO_3)_2$, $(NH_4)_2S$.

Following is a list of the elements which have thus far been discovered. The table includes not only the names of the elements, but their atomic symbols, atomic weights, —as determined by every available method,—and their specific gravities.

The small Roman numerals or indices added to the symbols are intended to indicate the *valence* (see Art. 158) of the elements. Usually the symbol is written without these.

25. A Table of the Elements.

Names.	Symbols.	Atomic Weights.	Physical condition at ordinary temperature.	Specific Gravity.
Aluminum	$\mathrm{Al}^{\prime\prime\prime\prime}$	27.	Solid	2.60
Antimony	$\mathrm{Sb}^{\prime\prime\prime,\mathrm{v}}$	120.	"	6.71
Arsenic	$\mathrm{As}^{\prime\prime\prime,\mathrm{v}}$	75.	"	5.73
Barium	$\mathrm{Ba}^{\prime\prime}$	137.	"	3.75
Beryllium	$\mathrm{Be}^{\prime\prime}$	9.	"	2.07
Bismuth	$\mathrm{Bi}^{\prime\prime\prime,\mathrm{v}}$	208.	"	9.80
Boron	$\mathrm{Bo}^{\prime\prime\prime}$	11.	"	2.5?
Bromine	$\mathrm{Br}^{\prime,\mathrm{v}}$	80.	Liquid	3.187
Cadmium	$\mathrm{Cd}^{\prime\prime}$	112.	Solid	8.60
Caesium	$\mathrm{Cs}^{\prime}$	133.	"	1.88
Calcium	$\mathrm{Ca}^{\prime\prime}$	40.	"	1.57
Carbon	$\mathrm{C}^{\prime\prime\prime\prime}$	12.	"	3.5–.6
Cerium	$\mathrm{Ce}^{\prime\prime\prime,\prime\prime\prime\prime}$	141.	"	6.68
Chlorine	$\mathrm{Cl}^{\prime,\mathrm{v}}$	35.5	Gas	2.450
Chromium	$\mathrm{Cr}^{\prime\prime\prime\prime,\mathrm{vi}}$	52.	Solid	6.50
Cobalt	$\mathrm{Co}^{\prime\prime,\prime\prime\prime\prime}$	59.	"	8.5–.7
Copper	$\mathrm{Cu}^{\prime\prime}$	63.3	"	8.95
Didymium	$\mathrm{D}^{\prime\prime\prime}$	142.3	"	6.54
Erbium	$\mathrm{E}^{\prime\prime\prime}$	166.	"	—
Fluorine	$\mathrm{F}^{\prime}$	19.	—	1.313
Gallium	$\mathrm{G}^{\prime\prime\prime\prime}$	69.	Solid	5.95
Gold	$\mathrm{Au}^{\prime,\prime\prime\prime}$	196.5	"	19.32
Hydrogen	$\mathrm{H}^{\prime}$	1.	Gas	0.069
Indium	$\mathrm{In}^{\prime\prime\prime\prime}$	113.6	Solid	7.42
Iodine	$\mathrm{I}^{\prime,\mathrm{v}}$	127.	"	4.948
Iridium	$\mathrm{Ir}^{\prime\prime,\prime\prime\prime\prime,\mathrm{vi}}$	193.	"	22.42
Iron	$\mathrm{Fe}^{\prime\prime,\prime\prime\prime\prime,\mathrm{vi}}$	56.	"	7.86
Lanthanum	$\mathrm{La}^{\prime\prime\prime}$	138.2	"	6.10
Lead	$\mathrm{Pb}^{\prime\prime,\prime\prime\prime\prime}$	207.	"	11.37
Lithium	$\mathrm{Li}^{\prime}$	7.	"	0.59
Magnesium	$\mathrm{Mg}^{\prime\prime,\prime\prime\prime\prime,\mathrm{vi}}$	24.	"	1.74
Manganese	$\mathrm{Mn}^{\prime\prime}$	55.	"	8.03
Mercury	$\mathrm{Hg}^{\prime\prime}$	200.	Liquid	13.55
Molybdenum	$\mathrm{Mo}^{\prime\prime,\prime\prime\prime\prime,\mathrm{vi}}$	96.	Solid	8.60
Nickel	$\mathrm{Ni}^{\prime\prime,\prime\prime\prime\prime}$	58.	"	8.90

Names.	Symbols.	Atomic Weights.	Physical condition at ordinary temperature.	Specific Gravity.
Niobium	Nb^{v}	94.	Solid	7.06
Nitrogen	$N^{\prime\prime\prime,v}$	14.	Gas	0.971
Osmium	$Os^{\prime\prime,\prime\prime\prime\prime,vi}$	199.	Solid	22.48
Oxygen	$O^{\prime\prime}$	16.	Gas	1.105
Palladium	$Pd^{\prime\prime,\prime\prime\prime\prime}$	106.	Solid	11.40
Phosphorus	$P^{\prime,\prime\prime\prime,v}$	31.	"	Colorless 1.83 Red 2.20
Platinum	$Pt^{\prime\prime,\prime\prime\prime\prime}$	195.	"	21.50
Potassium	$K^{\prime}$	39.	"	0.87
Rhodium	$Ro^{\prime\prime,\prime\prime\prime\prime,vi}$	104.	"	12.10
Rubidium	$Rb^{\prime}$	85.	"	1.52
Ruthenium	$Ru^{\prime\prime,\prime\prime\prime\prime,vi}$	103.5	"	12.26
Samarium	Sm	150.	"	—
Scandium	Sc	44.	"	—
Selenium	$Se^{\prime\prime,\prime\prime\prime\prime,vi}$	79.	"	4.50
Silicon	$Si^{\prime\prime\prime\prime}$	28.	"	2.39
Silver	$Ag^{\prime}$	108.	"	10.53
Sodium	$Na^{\prime}$	23.	"	0.978
Strontium	$Sr^{\prime\prime}$	87.5	"	2.54
Sulphur	$S^{\prime\prime,\prime\prime\prime\prime,vi}$	32.	"	2.05
Tantalum	Ta^{v}	182.	"	10.40
Tellurium	$Te^{\prime\prime,\prime\prime\prime\prime,vi}$	125.?	"	6.40
Terbium	Tb	148.5?	"	—
Thallium	$Tl^{\prime,\prime\prime\prime}$	204.	"	11.85
Thorium	$Th^{\prime\prime\prime\prime}$	232.	"	11.00
Tin	$Sn^{\prime\prime,\prime\prime\prime\prime}$	118.	"	7.29
Titanium	$Ti^{\prime\prime,\prime\prime\prime\prime}$	48.	"	—
Tungsten	$W^{\prime\prime\prime\prime,vi}$	184.	"	19.12
Uranium	$U^{\prime\prime\prime\prime,vi}$	239.8	"	18.70
Vanadium	$V^{\prime\prime\prime,v}$	51.5	"	5.50
Ytterbium	Yb	173.	"	—
Yttrium	$Y^{\prime\prime\prime}$	89.	"	—
Zinc	$Zn^{\prime\prime}$	65.	"	7.15
Zirconium	$Zr^{\prime\prime\prime\prime}$	90.	"	4.15

Rem. 1. Many elements occurring in the earth have also been discovered in the sun and stars.

Rem. 2. Some elements occur in such very small quantities that their properties are not accurately known; while others have been discovered so recently that they have not been fully investigated. (See Chem. News, Nov. 7, 1883, for List of Elements.)

Rem. 3. More elements will be discovered, undoubtedly; and some substances now known as elements may prove to be chemical compounds, as our chemical researches advance.

Sug. Student, learn to spell the names of the elements. Learn to give the symbol when the element is named, and *vice versa.*

Rem. 4. In estimating the specific gravity of the elements, *water* is taken as the standard for solids and liquids, while *air* is taken for gases.

Rem. 5. The chemist also uses *hydrogen* as a standard for estimating the density of gases, as will be explained later.

SUMMARY OF STUDENT'S WORK IN INTRODUCTION.

1. Make those experiments whose numbers are followed by the letter "P."

General Note. When "P" follows the number of an experiment, the student should be able to do the work: if, however, the student cannot do the work, owing to various causes for which no text can provide, or if the teacher wishes the work done differently, a few simple oral directions from the teacher to the class will assist greatly.

Experiments marked "T" are to be made by the teacher before the class. Let the pupils assist as much as possible.

In experiments marked "TP," it is advisable for the teacher to make the experiment for the class before requiring the student to do it.

Experiments marked "OP" are optional.

Encourage the student to exert his ingenuity in overcoming obstacles, and he will soon become quite independent in manipulation.

CHAPTER I.

OXYGEN: ITS OCCURRENCE, PREPARATION, PROPERTIES, AND TESTS. — OZONE.

THE ELEMENT OXYGEN.

SYMBOL O''. — ATOMIC WEIGHT, 16; SPECIFIC GRAVITY, 1.1056.

26. Occurrence. — Oxygen occurs well-nigh everywhere in nature. It constitutes 44 to 48 per cent of the weight of the earth's crust, 88.89 per cent of water, and about 23 per cent of the atmosphere.

Oxygen occurs in combination with every known element except fluorine.

27. Preparation. — EXP. 5 P. Heat one gram mercuric oxide, HgO, in a hard glass test-tube. The oxygen is driven off, while the mercury is condensed on the sides of the tube. Test the presence of the gas with a glowing match. ($HgO = Hg + O$.)

QUERY. Aug. 1, 1774, Joseph Priestley made this experiment for the first time. What gas did he discover?

EXP. 6 P. Minium, or red oxide of lead, Pb_3O_4, is to be heated as above. A part of the oxygen is driven from the red oxide of lead with great difficulty. ($Pb_3O_4 = 3\ PbO + O$.) Test as before.

SUG. Try $KClO_3$ with and without MnO_2, as above. Also heat, as above, $KClO_3$ with a pine splinter. What occurs? Explain.

QUERIES. Why does not the red oxide of lead, Pb_3O_4, part with its oxygen as readily as mercuric oxide, HgO? *Ans.* The lead has a stronger chemism for oxygen than mercury has. It is upon the principle of variable degrees of chemism existing between different substances, that double chemical reactions are always based. Do you obtain metallic lead in this experiment? Heat some red oxide of lead on charcoal, with sodium carbonate (Na_2CO_3), before the blow-pipe. Do you now obtain metallic lead? What effect do the sodium carbonate and charcoal have on substances treated thus? *Ans.* The charcoal abstracts oxygen from the oxide, or acts as a strong *reducing agent.* The sodium carbonate serves as a "flux," preventing the lead from again taking up atmospheric oxygen.

Oxygen can be prepared most easily from the compounds which it forms with other elements; as, mercuric oxide, HgO; manganese dioxide, MnO_2; potassium chlorate, $KClO_3$, etc.

Potassium chlorate, $KClO_3$, is the most available substance for preparing moderately large quantities in small laboratories; but if very large quantities are required, it may be prepared more cheaply from manganese dioxide, although special apparatus is necessary.

Potassium chlorate gives up its oxygen more readily and at a lower temperature when mixed with manganese dioxide ($KClO_3 = KCl + 3\,O$). The manganese dioxide is unchanged. This method is best for laboratory use.

EXP. 7 T. Pulverize 100^g *potassium chlorate*, $KClO_3$, and mix thoroughly with 25^g manganese dioxide, MnO_2. Place the mixture in an iron or copper retort, and arrange to wash the gas through two Woulff bottles: the first containing water, the second sodium hydroxide, NaOH. Now heat strongly but carefully, and, when the air is expelled from the apparatus (test with a match), connect with the gas receiver. Notice that at a certain point the gas is given off with great rapidity. The heat must be moderated immediately to avoid accident. You will thus obtain about 30^l of pure oxygen gas.

CAUTION. Organic matter or carbon, when present, may produce a serious explosion. It is best, therefore, to try a little of this mixture in a test-tube before heating the retort. Use C. P. materials.

NOTE. It is always best to have the class present when preparing such experiments as this last. Arrange the pneumatic trough, bell jars, wires, etc., and make the following experiments in a dark room.

28. Properties of Oxygen. — EXP. 8 T. Plunge into a jar of oxygen a glowing pencil of thoroughly charred bark charcoal. It will burn with brilliant scintillations. ($C + 2\,O = CO_2$.)

NOTE. This illustrates the combustion of fuel.

EXP. 9 T. Place a bundle of very fine iron wires, tipped with sulphur and ignited, in a jar of oxygen. The wires will burn with a reddish light, and at times with beautiful scintillations. ($3\,Fe + 4\,O = Fe_3O_4$.)

NOTE. This illustrates the great chemical activity of pure oxygen.

EXP. 10 T. File the end of a watch-spring till very thin. Draw the temper in a spirit-lamp, and uncoil it. Make a hook on the thin end, tip with sulphur, and ignite. Place in a jar of oxygen. The spring will burn with great energy. ($3\,Fe + 4\,O = Fe_3O_4$.)

EXP. 11 T. Place a piece of phosphorus in a jar of oxygen. Ignite. It burns with a brilliant white light. ($2\,P + 5\,O = P_2O_5$.) See Phosphorus.

EXP. 12 T. Treat a piece of sulphur as in last experiment. It burns with a violet light. ($S + 2\,O = SO_2$.)

NOTE. Do not allow the fumes from the burning of phosphorus and sulphur to escape in the room, as they are very disagreeable.

EXP. 13 T. Cut zinc foil into fine strips; make into a bundle; tip with sulphur; ignite. White light in oxygen. ($Zn + O = ZnO$.)

NOTE. The product formed is called "Philosopher's Wool."

Now that you have prepared and experimented with oxygen, you will be ready to appreciate several of its physical and chemical peculiarities which we term *properties.* Oxygen is an invisible, odorless, tasteless gas. Its specific gravity is 1.10563; and 1^l at 0° and 760^{mm} pressure weighs 1.430^g.

It has been liquefied by a pressure of 25.85 atmospheres at a temperature of −131.6°. (Read R. and S., p. 516, Vol. II., Pt. II.)

Exp. 14 op. Place a live mouse upon a cork raft, under a bell jar filled with air, over the pneumatic trough. Secure the jar so that no communication with the outside air is possible. Does the water rise in the jar? What does this indicate?

Queries. How does the oxygen come in contact with the blood? What harm ensues from persons living in a room without ventilation? Is the blood purified by a physical or chemical process?

Oxygen is that constituent of air which is essential to breathing, and all animals consume it. When inhaled, it enters into combination with some of the tissues of the body, actually burning them out, and thus liberating heat and energy. Air that has been breathed over too many times loses its vitality, the oxygen having been consumed.

As oxygen occurs in the atmosphere, it is largely diluted with nitrogen.

Exp. 15 op. Place a live fish in a sealed jar of water. What follows? Why?

Water absorbs free oxygen, and fishes consume this oxygen by means of their gills, which serve as lungs.

Query. How does a jet fountain render water fit for preserving the life of fishes?

Exp. 16 op. Place a burning taper in a closed jar of air. When the oxygen of the air is consumed, what occurs?

Queries. Why does blowing the fire cause it to burn more briskly? Why does blowing a candle extinguish it? (See next Exp.)

Fire or *Combustion* is produced by the union of the fuel with atmospheric oxygen. Before a substance can unite with oxygen, it must be heated to what is called its burning temperature or kindling point; and to produce flame, it must be converted into a gas. A flame is a burning gas.

Exp. 17 p. Carefully place a bent glass tube very near the wick of a lighted candle, within the flame zone. The gas escaping from the wick will be forced up through the tube, and may be lighted at the other end of the tube.

Since the gas which escapes from the wick burns only when mixed with air, the flame of a candle has but a thin outer zone, in which the gas is entirely consumed. (Fig. 1.)

Explanation of Fig. 1.

T, bent glass tube.
C, centre of unconsumed gas.
P, zone of incomplete combustion.
F, light zone, or zone of complete combustion.
F′, unconsumed gas burning at end of glass tube.

Queries. What does this experiment prove? Why can you not ignite a lump of anthracite coal with a match? Why does a blow-pipe give such a hot flame?

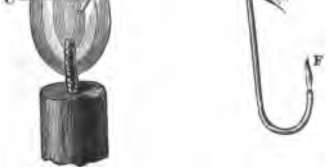

Fig. 1.

Bunsen Burner. — This burner is almost exclusively used in laboratories provided with gas for heating purposes. It gives a very hot, clean flame, owing to the fact that it is so arranged that the gas, before ignition, is thoroughly mixed with air, which insures its complete combustion. The tube *e*, shown in Fig. 2, is pierced with holes at its base, and the gas is discharged at about the height of these holes. Now, as the gas ascends the tube *e*, it draws a current of air along with it; the air and gas mix in their ascent through *e*, and burn with a hot, non-luminous flame when ignited at the top of *e*. A ring *a* pierced with holes surrounds *e*; by turning this ring, the holes *dd* may be closed, when the gas burns with an ordinary luminous flame, which is the flame used for the blow-pipe. And here the student may learn the meaning of the terms *Oxidizing Flame* and *Reducing Flame*, for which he will hereafter find frequent application. The way in which these flames are produced is as follows: —

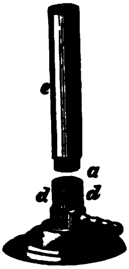

Fig. 2.

1. *The Oxidizing Flame.* — First close the openings *dd*, and make a moderately small luminous flame. Now place the tip of the blow-pipe *in the centre* of the luminous flame, and blow gently, using the *cheeks* like a bellows. The oxidizing flame should be non-luminous. In case you do not succeed in making it so, do not try to remedy the evil by blowing harder, which will end only in exhausting you, but moderate the flow of gas, and try again. After a little practice you should be able to keep the flame *steady* for half an hour, without becoming much fatigued.

This flame tends to oxidize substances when they are placed in it, since it contains an *excess of oxygen* at a very high temperature.

Queries. Whence comes this excess? Should air from the lungs be used in blow-piping? Why?

Sug. Examine a blow-pipe, and give a short description.

2. *The Reducing Flame* is made by placing the jet of the blow-pipe just *outside* of the luminous flame from the burner, with the openings closed. This flame is slightly luminous, and reduces or takes oxygen away from bodies placed in it, since it contains an *excess of hydrogen and carbon* (illuminating gas is a hydrogen-carbon compound) at a high temperature; both hydrogen and carbon have a strong affinity for oxygen.

Moreover, the bead, or assay, is to be kept within the zone of complete combustion (Fig. 1) when you are using the oxidizing flame; when using the reducing flame, the proper position of the assay is within the zone of incomplete combustion.

Query. If you use your *lungs* for bellows, can you keep the blow-pipe flames steady?

Exp. 18 p. Make a borax bead by fusing borax on a loop of platinum wire. *Slightly moisten* this bead in ferrous sulphate, $FeSO_4$, and heat a short time in the *oxidizing* flame. The bead thus treated should be of a reddish color when hot, fading to a light yellow when cold. Now heat the same bead persistently in the *reducing* flame. It should become colorless unless too strongly saturated with the ferrous sulphate, when it becomes pale green. Unless the proper flames are used, these results cannot be obtained.

Spontaneous Combustion. — The combination of oxygen and other substances always produces a definite amount of heat depending upon the nature of the substance. When iron rusts slowly, the heat is imperceptible; but when greasy rags or waste are thrown in a heap, the heat produced by the oxidation of the oils may, in time, be sufficient to raise the mass to the temperature of ignition. This kind of action, known as spontaneous combustion, is not unfrequently the cause of disastrous fires.

Exp. 19 p. Sift very fine iron-filings over the flame of an ordinary lamp. What results?

Query. Why is this? What does it illustrate?

Sug. Try fine dust from a malt house, flour mill, wood-working shop, etc., as above. The best place to collect the dust is from rafters or high beams. Why?

Fine dust collecting in the attics of large mills and malt houses has sometimes exploded when ignited, causing great destruction of life and property. Again, the sun's rays, when brought to a focus on inflammable substances, or steam pipes coming in too close proximity to inflammable substances, have produced unlooked-for conflagrations.

Exp. 20 p. Place green plant-leaves in the sunlight, under a bell jar filled with water. Bubbles of oxygen will collect at the top of the jar.

Oxygen is given off by plants growing in the sunlight. Enough oxygen is returned to the air in this way to keep its composition nearly uniform.

29. Tests for Free Oxygen. — 1. Char a small pine stick, as a match, and, with one end glowing, place it in a jar or current of free oxygen, when it will burst into flame.

2. Fill a flask with oxygen gas. Pour in a small quantity of potassium hydroxide, KOH. Shake, and no change in the liquid takes place. Then add a small quantity of pyrogallic acid, $C_6H_3(OH)_3$. Shake again, and the liquid turns brown, oxygen being absorbed.

N.B. In testing an unknown gas in this way, it is absolutely necessary to exclude all air, as the free oxygen of the air gives this reaction. It is best, therefore, to fill the flask over mercury. (See App.)

OZONE.

30. **Ozone** is a peculiar or allotropic form of oxygen found in the atmosphere, and produced by electrical discharges, or by evaporation, or by both. When an element occurs in more than one form, the unusual one is called an *allotropic* form. It is easily prepared by several methods.

31. **Preparation.** — Exp. 21 p. Place a small quantity of a solution of potassium permanganate, $K_2Mn_2O_8$, in a flask or test-tube. Add a few drops strong sulphuric acid, H_2SO_4. Notice the odor of the gas given off. It is ozone. Apply Test 1 for ozone.

Ozone may be prepared by suspending a clean stick of phosphorus in a closed jar containing a little water and atmospheric air at a temperature of 15° to 20°. Ozone is formed very rapidly.

When an electrical machine, in good working order, is in action, a peculiar odor is observed which is due to ozone. (Use Test 1, Art. 33, for ozone.)

Ozone may also be obtained by passing a silent electrical discharge, carefully avoiding sparks, through a closed jar of oxygen.

Sug. Produce ozone by one or all of the above methods.

32. **Properties.** — Ozone is three volumes of oxygen condensed to two volumes, the condensation being probably accompanied by some deep-seated change in the relation of the atoms.

There are good reasons for believing that the molecule (Art. 155) of ordinary oxygen consists of two atoms, as indicated by the formula O_2, and that the molecule of ozone should be represented by the formula O_3. Ozone is readily changed into ordinary oxygen. It is an active oxidizing agent. When brought in contact with mercury and some other substances in the dry state and at ordinary temperatures, it converts them into oxides, and itself becomes ordinary oxygen.

Ozone readily acts upon organic substances, and is supposed to destroy the germs of contagious diseases. When present in large quantities, ozone has an irritating effect on the lining membranes of the throat and nostrils, wherefore it should be dilute if inhaled.

Atmospheric ozone is more plentiful in the open country than in cities, and more is found out of doors than in dwellings. (Why?)

NOTE. It is extremely difficult to determine whether the substance in the atmosphere which is commonly called *ozone*, is really ozone or not. There are certainly other substances present which in some of their properties closely resemble it; such, for example, as hydrogen dioxide (Art. 44).

33. **Tests for Ozone.** — 1. A paper strip saturated with a solution of starch paste and potassium iodide, KI, turns blue when exposed to the action of ozone.

REM. This test is the one employed to determine the presence and amount of ozone in the atmosphere; but it is not reliable, since some of the oxides of nitrogen, which also exist in the atmosphere, affect the paper similarly.

2. Its odor, resembling dilute chlorine, betrays ozone when present in considerable quantities.

3. Metallic mercury, Hg, when dropped into a flask containing ozone, immediately tarnishes.

SUMMARY OF STUDENT'S WORK IN O. AND OZONE.

1. Make the experiments as indicated.
2. Make Tests 1 and 2, Art. 29; also test a flask of common air by 2.
3. Make Tests 1, 2, and 3, Art. 33; also fit a delivery tube to the florence flask used in Exp. 21 P, and direct the jet of ozone against a globule of Hg in the bottom of a test-tube. What result?
4. Allow the jet of ozone to pass into a test-tube containing a solution of starch paste and KI. What occurs?
5. Read R. and S., Vol. I., p. 194, et seq., for a more complete discussion of ozone.
6. Read *Huxley's Elementary Lessons in Physiology* on the arterialization of the blood.
7. The manganese bead (Art. 316) will furnish the student excellent practice in the use of the oxidizing and reducing flames.
8. Will ozone give the oxygen test with the glowing match? How can you distinguish between ozone and oxygen?

CHAPTER II.

HYDROGEN. — ITS OCCURRENCE, ETC. — WATER. — HYDROGEN DIOXIDE.

HYDROGEN.

Symbol H'. — Atomic Weight, 1; Specific Gravity, 0.0692.

34. Occurrence. — Hydrogen is found, nearly always, combined with other substances. It occurs free, however, in very small quantities in certain volcanic gases, and absorbed in meteorites.

It occurs combined with oxygen in the form of water, of which it constitutes 11.11 per cent by weight.

It is a constituent of ammonia, coal gas, marsh gas, and of nearly all organic substances.

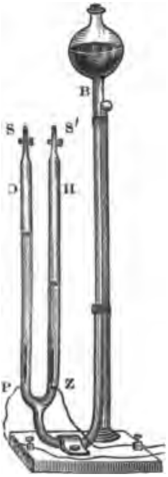

Fig. 3.

35. Preparation. — Exp. 22 t. Use the apparatus shown in Fig. 3. Add 1 part by weight of pure sulphuric acid, H_2SO_4, to 20 parts distilled water; then open the stop-cocks S and S'. Pour the acidulated water into the tube B until it issues from the tubes O and H. Then close the stop-cocks, and fill B up to the bulb. Connect the platinum wire Z, which is melted through the tube H, and terminates in a platinum strip, with the zinc pole of a Grove's battery consisting of five or six cells. Also connect the platinum wire P (which is like Z in every respect) to the platinum pole of the battery. Hydrogen collects in tube H, and oxygen in tube O. The hydrogen in tube H may be tested by slightly opening the stop-cock S′, and igniting. Hydrogen burns with a very hot flame, although it emits but little light.

Queries. In which tube is the volume of gas greater? How test the oxygen?

Exp. 23 T. Make an amalgam by rubbing, in a porcelain mortar, one-half gram metallic sodium, or potassium, together with 5^g mercury.

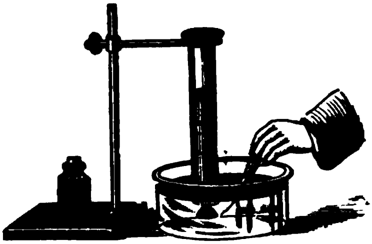

Fig. 4.

Fill a jar with water, and arrange as in Fig. 4. Place the amalgam in a wire gauze cage, and insert under the mouth of the jar. Hydrogen is liberated, which rises, and fills the jar.

Test by carefully raising the jar, mouth downwards, and plunging a lighted taper upward into the jar. The taper is extinguished, but the hydrogen burns at the mouth of the jar. The taper may be relighted in this flame.

Note. This experiment usually ends with a slight but not dangerous explosion.

Queries. What becomes of the mercury of the amalgam after being dipped into the water? Drop a piece, not larger than a pea, of metallic sodium or potassium into a dish of warm water. What results? Do you now see the reason for amalgamating the K or Na? What is the reason? Is the water alkaline?

Note. Alkalies turn a strip of red litmus paper, blue. Acids turn blue litmus paper, red.

Hydrogen is best prepared in a pure state by the decomposition of water. It may be prepared in many other ways; but it then contains impurities from which it is difficult to free it.

The action of potassium on water is expressed by the equation

$$K + H_2O = KOH + H.$$

Now let us inquire particularly as to the meaning of an equation. Primarily, it means that potassium *and* water *give* a substance called potassium hydroxide (KOH) and hydrogen. It will be seen that the sign + is read *and*, and the sign = is read *give*. But the equation means more than this. It tells us the exact proportions in which the substances act. For each one of the symbols stands for a certain proportion of the element corresponding to its atomic weight. In the above, 39 parts of potassium act upon 18 parts of water (made up of 2 × 1 parts of hydrogen and 16 parts of oxygen), and give the compound potassium hydroxide (made up of 39 parts of potassium, 16 parts of oxygen, and 1 part of hydrogen), and 1 part of hydrogen. These relations are maintained whenever potassium acts upon water. From the use of a given amount of potassium, provided there be enough water, we get a definite amount of hydrogen.

PROBLEM. How much hydrogen will be formed if 100^g of potassium were allowed to act upon water in such a way as to prevent the burning of the hydrogen? How much potassium hydroxide will be formed? How much water will be decomposed?

SUG. Teacher will give a number of other similar problems, calling attention to the fact that instead of saying *parts* we may say grams, ounces, pounds, tons, or whatever unit of weight we may choose to take. Student review the equations inclosed in parentheses, and explain.

Exp. 24 t. Place a quantity of granulated zinc in the generating flask A, Fig. 5. Through the funnel tube B introduce a liberal quantity of dilute sulphuric acid, H_2SO_4, consisting of one part acid by weight to four of water. Allow the gas to escape through the delivery tube D for some time, to free the apparatus from air. Then collect in gas bags, or in the gas receiver, or in jars over the pneumatic trough. The reaction is represented by the equation

$$Zn + H_2SO_4 = ZnSO_4 + 2\ H.$$

We take no account of the water added, as it serves merely as a solvent for the zinc sulphate, $ZnSO_4$, as fast as formed.

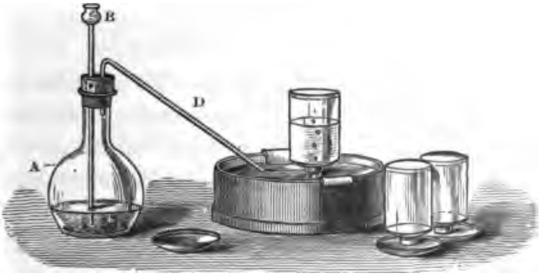

Fig. 5.

Hydrogen is prepared in large quantities, when absolute purity is not especially requisite, by allowing dilute acids (HCl, H_2SO_4) to act on certain metals, such as iron and zinc.

Note. Hydrogen made in this way may contain sulphuretted hydrogen and other impurities, which, for the most part, are destroyed by passing the gas through a solution of potassium permanganate. The gas may be dried by passing it through sulphuric acid or calcium chloride, or both. (Student should arrange an apparatus for making and purifying hydrogen.)

Having a quantity of hydrogen stored, teacher and students make the following experiments: —

36. Properties. — Exp. 25 P. Fill collodion balloons to illustrate the lightness of hydrogen. Allow one or two of them to rise to the ceiling, and remain as long as they will. Even though they do not leak, they will, nevertheless, sink to the floor after a time. Why?

Exp. 26 TP. Make hydrogen soap-bubbles, which will burn when touched with the flame of a taper.

Queries. Are these bubbles heavier or lighter than air? How can you tell the same of other gases?

Exp. 27 TP. Discharge the hydrogen pistol, illustrating the explosiveness of hydrogen and oxygen.

Query. Should you fill the pistol full of H, could you discharge it? Why?

Exp. 28 TP. Produce singing flame. To succeed well with this, fit a long, straight jet into a generating flask containing metallic zinc and dilute sulphuric acid. When the gas is coming off freely, light the jet. Hold glass tubes of various lengths and bores, down over the burning jet. In this way different tones may be produced.

Query. What produces the tones?

Exp. 29 TP. Fill a bell jar with hydrogen, by holding the mouth of the jar downward, and allowing the hydrogen to flow up into the jar. Now reach up into the jar with an inverted dipper (ordinary). Keeping the dipper bottom side up, draw it slowly downward out of the jar, and remove it some distance away; then bring a lighted taper under the dipper. What ensues? Explain.

Pure hydrogen is an odorless, tasteless, invisible gas, which was discovered and described by Cavendish in 1766.

Its specific gravity (air = 1) is 0.0692. Hydrogen is the lightest substance known: 1^{l} at 0° C. and 760^{mm} pressure, weighs 0.0896^{g}.

Prob. How many grams H, at 0° and 760^{mm}, will a bell jar of 20^{l} capacity hold?

M. Pictet claims to have liquefied hydrogen at —140° C., and 650 atmospheres; but the so-claimed liquid gave no meniscus in the tube in which he was endeavoring to condense the gas.

Sug. Student, half fill a test-tube with water, and note the meniscus at the upper level of the liquid.

Hydrogen is highly combustible, burning with a very hot but slightly luminous flame, and, when mixed with considerable quantities of air or free oxygen, explodes with violence.

The metal palladium absorbs hydrogen in large quantities at moderate temperatures. Platinum and iron also absorb it, but in much smaller proportion than palladium. It seems as if the hydrogen forms an alloy with them, acting very much like a metal itself. When a jet of hydrogen is directed against a piece of spongy platinum, at ordinary temperatures, so much heat is evolved as to cause the jet to ignite. Hydrogen is slightly soluble in water. It is not directly poisonous, but produces a weakening and sharpening effect on the voice, when inhaled. It is very diffusible, and is apt to contain atmospheric air. The extreme lightness of hydrogen caused it to be used for filling balloons; but, owing to its great diffusibility and the expense of its manufacture, it has been superseded by coal-gas. One gram of hydrogen, when burned, produces enough heat to raise the temperature of 34,462^{g} of water through one degree. Hence its calorific power is said to be equal to 34,462 thermal units, —the thermal unit or *Calorie* being the amount of heat necessary to raise the temperature of one gram of water one degree Centigrade.

37. Test. — Hydrogen may be recognized by its *flame* and behavior, as in the preceding experiments.

HYDROGEN AND OXYGEN COMPOUNDS.

38. Hydrogen and **Oxygen** form two chemical compounds; viz.: —

1. Water, H_2O; and
2. Hydrogen dioxide, H_2O_2.

WATER, H_2O.

39. Occurrence. — With water we are all well acquainted. It occurs everywhere, — in streams, lakes, and the boundless ocean. It exists in the atmosphere as vapors, fogs, and clouds, and is precipitated upon the earth as dew, rain, hail, and snow. It is absorbed by the soil and rocks, while in crystalline structures it enters into closer combination as water of crystallization.

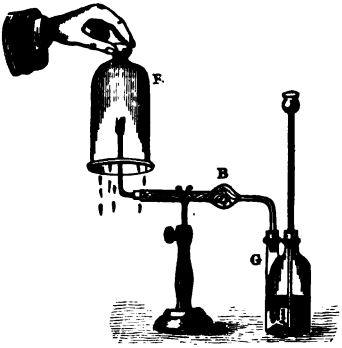

FIG. 6.

40. Preparation. — It is not necessary to prepare water chemically, owing to its great abundance everywhere, but for the sake of illustration use the apparatus shown in Fig. 6.

G is a hydrogen generator.

B is a drying bulb, containing granulated calcium chloride.

R is a bell jar. The hydrogen jet burning in this jar unites with the oxygen of the air, producing water, which soon collects, and falls down in drops.

Sug. Student, write the equation. Also write a description of the whole apparatus and manipulations.

41. Question. — What is the chemical composition of water, and what its formula?

We may determine the composition of water, first by analysis, and then, if possible, by synthesis. The experiment described on page 34 showed that when water is decomposed by the electric current, it yields only hydrogen and oxygen, and these in the proportion of 2 volumes of hydrogen to 1 of oxygen. Knowing the relative weights of the gases, we see that they are obtained from water in the proportion of 1 part by weight of hydrogen to 8 of oxygen, or 2 of hydrogen to 16 of oxygen.

Sug. Student, show that this statement is correct.

To prove that hydrogen and oxygen alone are necessary to form water, and that they are present in the proportions found by analysis, we may cause the two gases to unite as follows: —

Exp. 30 tp. The apparatus shown in Fig. 7 is called *Ure's Eudiometer*. The graduated limb and part of the plain limb are filled with mercury; then, by means of a curved tube, 10 divisions of the graduated limb are filled with pure oxygen; then fill say 25 more with pure hydrogen. An electric spark is now passed through the wires attached to the graduated limb, while the thumb is held firmly over the plain limb. 20 divisions of hydrogen will unite with 10 divisions of oxygen; *i.e.*, 2 of hydrogen to 1 of oxygen.

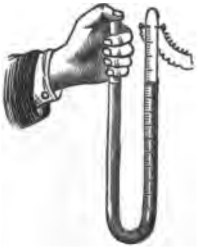

Fig. 7.

Query. After passing the spark, where is the water to be seen?

N.B. Before passing the spark, see that the plain limb is not entirely full of mercury, and hold the thumb as firmly as possible.

Sug. Student, examine this apparatus, and write a full description of it and the experiment.

We see, thus, that the analysis and synthesis of water both lead us to the conclusion that in it hydrogen and oxygen are united in the proportions above stated, and these proportions are expressed in the formula H_2O, the full significance of which cannot be explained at this stage. For the present, suffice it to say that formulæ express primarily the composition of bodies by weight. Hereafter, we shall see that they also have to deal with the volumes of bodies when in the form of a gas.

Prob. How many grams of O in 100^g of H_2O? How many of H?

42. The Oxy-Hydrogen Blow-Pipe. — Small laboratories will not be likely to contain this apparatus; but, owing to its great value and the frequent references made to it, the student should become acquainted with it.

The oxygen and hydrogen holders are not shown in this cut (see App.). They may be provided with safety-valves, to prevent the flow of the gas from one to the other.

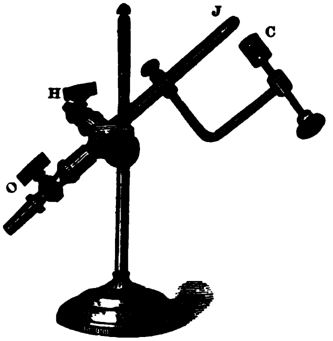

Fig. 8.

J is a jet containing a jet within, a space being left between the inner jet and the outer one for hydrogen to pass through.

H is a stop-cock to admit hydrogen into this space. O is a stop-cock to admit oxygen into the inner jet, which is not quite so long as the outer jet. By this arrangement the two gases are thoroughly mixed upon issuing into the air.

C is an adjustable cup for holding a piece of chalk in the flame, when the design is to produce the brilliant calcium light.

The heat of the flame of this blow-pipe is intense enough to melt most of the refractory metals.

The calcium light is equaled only by the electric light.

43. **Properties of Water.** — Water is an almost universal solvent; consequently, pure water does not occur in nature. Snow and ice waters are nearly pure, but they still contain dust, and various gases found in the air. Lake Superior water is also very nearly pure, since the bed of the lake is composed of the old Azoic rocks which are but slightly soluble, and the lake is fed with ice, snow, and rain. Sea water contains nearly every known substance in solution.

Water is at its maximum density at +4° Centigrade. When the temperature passes either above or below this point, water expands. This is a most fortunate provision, as otherwise, ice would be heavier than water and would *sink to the bottom;* thus, many of our lakes and rivers might be frozen solid to their beds, and the summer sun would not suffice to thaw them. Aquatic plants and animals could not exist, and our temperate zones would become uninhabitable.

QUERY. Why does the pail burst when the water freezes in it?

EXP. 31 OP. Place a thermometer through an opening in the ice of a frozen lake. At any depth it will read nearly +4° C.

QUERY. What deductions may be derived from this experiment?

THE LATENT HEAT OF WATER IS 79 CALORIES OR THERMAL UNITS.

Illustrate this statement, thus: —

EXP. 32 OP. Mix 1^k of ice at 0° C. with 1^k of water at 79° C. The ice will melt, and the temperature of the 2^k of water will be 0° C. Hence we see that the 79 thermal units contained in the kilogram of water have disappeared while melting the ice, or, in other words, have become *latent*. When water freezes, it gives off its latent heat.

QUERY. What effect, upon the temperature of a room, would be produced by a tank of freezing water.

THE LATENT HEAT OF STEAM IS 536 THERMAL UNITS.

To illustrate this, proceed thus: —

EXP. 33 OP. Into 5.36^k of water at 0° C. pass steam at 100° C. until the water boils. You will then have 6.36^k of water at 100° C. Now, since 1^k of steam has parted with sufficient *latent heat*, while condensing to water (of the same temperature, *i.e.*, 100°), to raise 5.36^k of water 100°, or 536^k 1°, we have measured its latent heat, which is 536 thermal units.

NOTE. Experiments 32 P and 33 P involve quite large experimental errors.

When steam condenses to water it gives off all its latent heat; hence its great usefulness for heating dwellings, etc.

DRINKING-WATER.

Drinking-water is apt to contain many impurities, organic and inorganic, some of which are believed to be very deleterious to health, frequently leading to various forms of disease, such as typhoid fever, etc.

QUERY. How does drinking-water become contaminated with impurities?

Let the student make the following tests upon drinking-water obtained from his own well, or from the usual source of water for drinking purposes.

TESTS FOR IMPURITIES IN DRINKING-WATER.

EXP. 34 P. *For Organic Impurities.* — Fill a tall glass jar with the water to be tested. Add a few drops of sulphuric acid, H_2SO_4; then add a solution of potassium permanganate, $K_2Mn_2O_8$, until the whole assumes a deep purplish tint. Stand in a warm place for one hour. If organic impurities are present, the solution will be decolorized.

Another Test. — When *much* organic matter is present. — Fill a tightly-stoppered bottle nearly full of the water to be tested. Set in a warm place for several days. An offensive odor indicates organic impurities. *Such impure water, it is dangerous to drink.* A good charcoal and gravel filter will remove organic impurities if only a *small* amount be present.

SUG. Teacher explain the construction of a filter, and how to take care of it.

TEST FOR AMMONIA.

EXP. 35 P. Distil the water in *perfectly clean* glass apparatus (after dissolving a small quantity of sodium carbonate, Na_2CO_3, in the water to be tested).

Collect the distillate in tall glass jars in volumes of 50^{cc} each, numbering them successively 1, 2, 3, 4, etc.

Add about 2^{cc} of Nessler's Test Solution (see App.) to each of these jars. If ammonia be present in any or all of them, such as contain it will be tinged brownish-yellow.

N.B. Drinking-water containing much ammonia is unfit to drink, since the presence of ammonia indicates that the water of the well has percolated through decaying vegetable or animal substances.

TEST FOR CHLORINE OR CHLORIDES.

EXP. 36 P. Concentrate 50^{cc} of water to be tested to 25. Acidulate with nitric acid; then add a few drops of a solution of silver nitrate, $AgNO_3$. If a white precipitate is made which is soluble in ammonia, NH_4OH, and insoluble in nitric acid, HNO_3, chlorine is present.

The presence of much chlorine is to be looked upon with suspicion (as sewage water always contains chlorine in considerable quantities), unless in the vicinity of salt wells or of the ocean.

TEST FOR NITRITES.

EXP. 37 P. Acidify the water to be tested with acetic acid, $H(C_2H_3O_2)$; then distil in a clean glass retort, allowing the first part of the distillate to drop into a solution of starch paste and potassium iodide, KI, to which a few drops of sulphuric acid, H_2SO_4, have been added. Nitrites, if present, will turn this solution blue, owing to the liberation of iodine.

NOTE. Nitrites will also bleach a solution of potassium permanganate, $KMnO_4$, when acidulated with sulphuric acid, H_2SO_4; but this test is not reliable, since organic matter acts in the same way.

The presence of nitrites is an indication of sewage, especially when chlorides and ammonia are present.

Too much stress cannot be laid on the danger of drinking water contaminated with sewage. Fevers and pestilence may follow its use.

TEST FOR HYDROGEN SULPHIDE, H_2S.

EXP. 38 P. Acidify, with sulphuric acid, H_2SO_4, about 1^l of the water to be tested. Place it in a stoppered flask holding say 2^l. Suspend above the liquid a strip of bibulous paper moistened with lead acetate, $Pb\ (C_2H_3O_2)_2$. Cork tightly, and set in a warm place for several hours. Hydrogen sulphide, if present, will blacken the paper.

TEST FOR HARDNESS.

EXP. 39 P. Employ Clark's Soap Test thus: Place 70^{cc} of the water to be tested in a stoppered glass flask. Add 1^{cc} of Clark's Soap Solution; then shake thoroughly. If a permanent lather be not formed, again add 1^{cc} of the soap solution, and shake as before, and thus proceed until a permanent lather remains, for three minutes, unbroken over the surface of the water. (See App. for Clark's soap solution.)

The number of centimetres soap solution added will be equal to the number of degrees of hardness, or to the number of grains plus one of hardness, per imperial gallon. Hardness is usually caused by the presence of calcium and magnesium carbonates.

NOTE. Hardness and hydrogen sulphide do not necessarily impair the qualities of drinking-water; on the contrary, they often serve useful purposes.

HYDROGEN DIOXIDE, H_2O_2.

44. Preparation. — Hydrogen dioxide does not occur in nature in quantity, though it is present in small amounts in the air, and in rain and snow. It may be prepared chemically in several ways, of which we give only one, the best way.

EXP. 40 P. Treat pulverized barium dioxide with dilute sulphuric acid (5 parts water to 1 part acid) in a beaker. Stir thoroughly to bring all the barium dioxide in contact with the acid. A white precipitate, barium sulphate, $BaSO_4$, will settle to the bottom upon standing, and the clear fluid will contain the hydrogen dioxide. This separation can be effected more quickly by filtering. The clear fluid which comes through contains the hydrogen dioxide in dilute solution. The reaction may be expressed thus: $BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$.

PROB. How many grams H_2O_2 may be obtained from 10^g BaO_2?

This dilute solution of hydrogen dioxide may be concentrated by allowing it to stand in a beaker placed over strong sulphuric acid in the vacuum of an air-pump; but, after and during concentration, it should be kept at a low temperature.

45. Properties. — Hydrogen dioxide is a very unstable liquid, slowly separating into water and oxygen at low temperatures (student, write the equation), rapidly decomposing at +20°, and exploding with violence at 100°.

It is syrupy, transparent, and colorless, possessing a very nauseating and stringent taste.

Its specific gravity is 1.452, and it has not been frozen.

Aqueous hydrogen dioxide is sold commercially for bleaching old engravings and paintings. It is also used to change dark hair to lighter shades, which is a dangerous practice, since it is an active poison when brought upon the skin, often producing white blisters which finally become very painful.

46. Test for Hydrogen Dioxide. — Acidulate a small quantity of a solution of hydrogen dioxide (or the liquid to be tested) with two or three drops of sulphuric acid, H_2SO_4, in a test-tube. Add a small quantity of ether, $(C_2H_5)_2O$, also five or six drops of potassium chromate, K_2CrO_4; shake well. Hydrogen dioxide, when present, turns the whole to a splendid blue color. On standing, the ether absorbs this color, and separates out in a blue layer.

SUMMARY OF STUDENT'S WORK IN H, H_2O, AND H_2O_2.

1. Make the experiments as indicated.

2. If the laboratory contain an oxy-hydrogen blow-pipe, teacher and students should use it in making the calcium light, fusing bits of metals, as Fe, Au, Pt, etc.

3. Art. 43. Draw up reports giving results of the Exp. 34 P–39 P. This is work sufficient for a whole week.

4. *Albuminoids* may be detected thus: Add solid KOH to the water until strongly alkaline, and boil a short time. Now pour into a retort and add $K_2Mn_2O_8$, and distil, collecting and testing the first portions of distillate as in Exp. 35 P, since albuminoids thus treated yield ammonia.

5. Read Wanklyn's *Water Analysis*. In case it is desirable to determine the *amounts* of ammonia, etc., present in drinking-water, complete directions are to be found in this work. One should hesitate to pronounce upon the potableness of drinking-water without first making quantitative determinations.

6. PROB. The imperial gallon contains 70,000 gr. of distilled water; the U. S. gallon contains 58,328.88 gr. How many grains of hardness per U. S. gallon does the sample of water that you have analyzed contain? How many milligrams per litre does it contain (1^{cc} Clark's soap solution precipitates 1^{mg} of hardness)?

7. Try to remove, by boiling, the hardness from a sample of water. In case you succeed, the hardness is said to be *temporary*; and it is due to the presence of calcium carbonate, $CaCO_3$, and perhaps magnesium carbonate, $MgCO_3$. Should you not succeed in thus removing it, the hardness is called *permanent*, and probably consists of the sulphates of calcium and magnesium.

QUERY. How can you determine if both permanent and temporary hardness be present?

8. PROB. How many grams O can be obtained by decomposing 100^{cc} of water ($1^{cc} = 1^{g}$)? How many grams H?

9. PROB. In the equations enclosed by parentheses, assume 10^{g} of the first substance, and ascertain how many grams will be required of the remaining substances.

10. Art. 44. It is not necessary to condense H_2O_2 in vacuo, unless a concentrated solution is required.

Student test H_2O_2, as in Art. 46. A dilute solution of H_2O_2 will answer well for this purpose. Use $K_2Cr_2O_7$, also, in place of K_2CrO_4. Do you obtain the same color as before?

CHAPTER III.

NITROGEN.—ITS OCCURRENCE, ETC.—AMMONIA.—OXIDES OF NITROGEN.—THE NITROGEN ACIDS.—HYDROXYLAMINE.

NITROGEN.

SYMBOL, N'''.—ATOMIC WEIGHT, 14; SP. GRAV., 0.9713.

47. Occurrence.—Nitrogen occurs free in the atmosphere, of which it constitutes nearly four-fifths by volume, or 77 per cent by weight. It also occurs in many chemical compounds, such as potassium nitrate, KNO_3; sodium nitrate, $NaNO_3$; ammonia, NH_3; and in many organic substances, particularly those of animal origin.

48. Preparation.—EXP. 41 T. Place in an iron sand-bath about 2^g of phosphorus; ignite the phosphorus, and float the sand-bath on the water in a pneumatic trough. Immediately place over the burning phosphorus a bell-jar of about 4^l capacity, allowing the mouth of the jar to be under water, so that no outside air can enter. The phosphorus enters into combination with the oxygen of the air contained within the jar, forming dense white fumes of phosphorus pentoxide, P_2O_5, and perhaps of the trioxide, P_2O_3. In a short time these fumes settle, and are dissolved by the water, leaving the nitrogen nearly pure.

Nitrogen may be prepared in many ways, but the method above indicated is a cheap and convenient one for laboratory use.

49. Properties of Nitrogen. — **Exp. 42 p. Bend a small glass tube in the shape of a letter V, and draw out one extremity into a jet. Now insert the plain end of the tube into the jar of nitrogen obtained in Exp. 41, and press the jar down into the water of the pneumatic trough until the nitrogen issues through the jet. Try to ignite the gas. Does it burn?**

Exp. 43 p. Fill with nitrogen a large test-tube. Insert a glowing match; a burning match; a lighted taper. What results?

Exp. 44 p. Try to fire the hydrogen pistol when filled with a mixture of nitrogen and common air. What occurs?

Nitrogen is a gaseous element, and, like hydrogen and oxygen, none of its physical properties render it perceptible to sight, taste, or smell. Its specific gravity is 0.971; and 1^l at 0° C. and 760^{mm} pressure weighs 1.256^g.

Chemically considered, it is not an active element, as shown by the apathy which it exhibits in entering into combination with other elements.

Indirectly, however, it unites with hydrogen, oxygen, and carbon to form important chemical compounds.

Its greatest value in nature is due to its mildness, and the remarkable persistency with which it remains in a free state. It thus serves to dilute the oxygen of the atmosphere, which is simply a mechanical mixture of these gases, consisting of 23.1 parts oxygen and 76.9 parts nitrogen, by weight. As one would infer, it has no poisonous properties, neither will it burn nor support combustion.

Nitrogen is but slightly soluble in water, and has been condensed to a liquid at − 146° C. and under a pressure of 33 atmospheres.

50. Test for Nitrogen. — Owing to its passive nature, nitrogen does not give any reaction whereby it may be readily detected when present in small quantities. Larger amounts are indirectly tested by the negative results obtained.

NITROGEN AND HYDROGEN.

51. Ammonia. — Nitrogen and hydrogen unite to form an important compound, viz.: —

AMMONIA, NH_3.

52. Occurrence. — Ammonia occurs free in the atmosphere, being produced by the decay of organic matter containing nitrogen. It is also found dissolved in small quantities in rain water and many surface waters. Its compounds, such as ammonium chloride, NH_4Cl, and ammonium carbonate occur but sparingly in nature, although they are common articles of commerce, obtained by artificial processes. Ammonia solution, or *aqua ammoniae*, is also a staple article of commerce.

53. Preparation. — EXP. 45 P. Place in one hand a small quantity of dry quicklime, CaO, and in the other an equal bulk of pulverized ammonium chloride, NH_4Cl. Note that neither substance emits an odor. Now rub them together between the palms of the hands, and carefully smell the invisible gas given off. It is ammonia.

EXP. 46 P. To a solution of ammonium chloride in a test-tube add a few drops of potassium hydroxide, KOH. Warm gently, and note the fumes. Do you again obtain ammonia? Also try in the same way a solution of ammonium nitrate, NH_4NO_3. What result? Moisten a glass stirring-rod with hydrochloric acid, HCl, and hold it in the escaping vapors; notice the white fumes that are formed. Try the same with nitric acid, HNO_3. What takes place is indicated in the two following equations: —

$$1.\ NH_3 + HCl = NH_4Cl.$$
$$2.\ NH_3 + HNO_3 = NH_4NO_3.$$

SUG. Explain these equations. Do you obtain the same substances with which you commenced?

EXP. 47 T. Thoroughly mix two parts, by weight, of finely-pulverized, dry ammonium chloride, and one part of dry quicklime. Quickly place the mixture in the generating-flask F (Fig. 9), and then add a thick layer of dry quicklime, which will serve to dry the ammonia as it rises through it. Insert the cork containing the bent tube, and gently heat the flask. Ammonia will collect in the bottle B.

This method is used when *dry* ammonia gas is required. What occurs in the flask is indicated by the equation,—

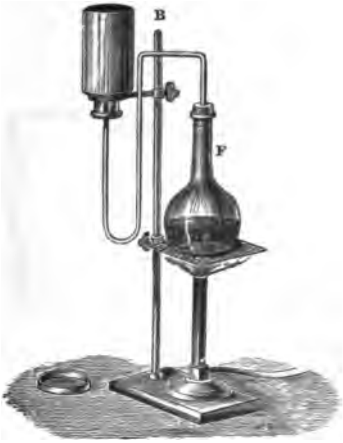

FIG. 9.

$$CaO + 2\,NH_4Cl = 2\,NH_3 + H_2O + CaCl_2.$$

QUERIES. $CaCl_2$ is a substance called calcium chloride, and is a solid. Where is it to be found after the reaction? What becomes of the water? Would passing the gas through a long tube filled with quicklime tend to insure the dryness of the ammonia? From the position in which the bottle B is held, should you judge ammonia to be lighter, or heavier, than air?

EXP. 48 T. Prepare thick pastes (with water) of the same substances used in the last experiment, employing the same proportions of the dry substances before moistening. Arrange an apparatus similar to that shown in Fig. 10. The first wash-bottle, A, acts as a safety-valve to prevent water from return-

ing into F; also to prevent explosions. Notice that the centre tube alone dips beneath the water. The bottle B contains cold water, and serves as a condenser. In this bottle the entry and centre tubes extend below the surface of the water. C is also a bottle containing cold water. It is best to place B and C in vessels, and to surround them with a freezing mixture of snow, or pounded ice and salt. Now pour these pastes as rapidly as possible into F, shake quickly, and connect with the wash-bottles. Apply heat to F, and boil for some time. An aqueous solution of ammonia will be found in B and C.

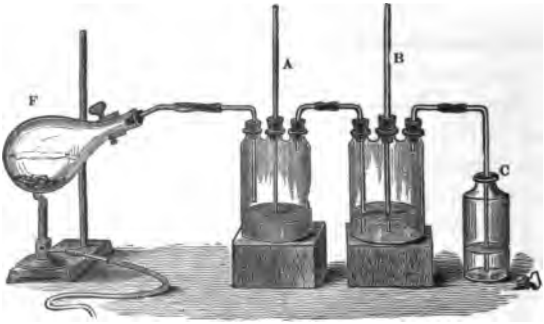

FIG. 10.

SUG. **Explain the reasons for arranging A in the manner described. After the experiment, note that the contents of B and C differ in no way from ordinary** *aqua ammoniae.*

The last experiment indicates the general process employed in manufacturing commercial *aqua ammoniae.*

Other methods of preparing ammonia are as follows:—

1. Ammonia is obtained in small quantities by mixing nitrogen and hydrogen in a eudiometer, and by passing for some time a silent electric discharge.

QUERY. **How does this explain the production, at certain times, of ammonia in the atmosphere?**

2. It is produced by allowing heaps of compost and urine to decompose.

QUERY. How do you explain the presence of ammonia in stables?

EXP. 49 P. Heat in a test-tube a small ball of hair, or wool, or a few hoof-clippings. What is given off?

3. Ammonia may be had by the dry distillation of such nitrogenous bodies as hair, hoofs, hides, and horns. It was formerly prepared in this way, and thus received the name *spirits of hartshorn.*

4. In the distillation of coal to make illuminating gas, ammonia is formed as a by-product. In this case the nitrogen and part of the hydrogen contained in the coal are driven off, combined as free ammonia and ammonia compounds. These ammoniacal products are led into water containing hydrochloric or sulphuric acids; from the compounds thus formed we obtain the ammonia of commerce.

54. **Properties.** — EXP. 50 P. Place in a generating-flask a concentrated solution of ammonia; pass through this solution a current of oxygen gas. The escaping mixture of ammonia and oxygen will burn, at the mouth of the flask, with a yellowish flame. Under ordinary conditions, ammonia does not burn.

SUG. Student, try to light a jet of NH_3.

EXP. 51 P. Heat to bright redness a long spiral coil of platinum wire, and quickly introduce it into the mouth of a common reagent bottle containing a strong solution of ammonia. The wire will continue to glow while the ammonia is decomposed, thus: —

$$2NH_3 + 3O = NH_4NO_2 + H_2O.$$

QUERIES. How do you account for this phenomenon? Whence comes the O indicated in the above equation?

The composition of ammonia gas may be determined by introducing the dry vapor into the graduated limb of Ure's eudiometer, and passing a succession of electric sparks, when the volume of the enclosed gas is doubled. This may now be proven, by introducing oxygen and exploding, to consist of one volume of nitrogen and three volumes of hydrogen.

We may here learn a useful fact; viz., *that the formula* NH_3, *in addition to its other significations, also represents two volumes of ammonia in the form of a gas; and the same is true of all formulas representing gases.*

The name *ammonia* originated from the fact that the gas was first prepared from *sal-ammoniac*, NH_4Cl, a substance formerly confounded with the salt, NaCl, produced near the ruins of the temple of Jupiter Ammon, in Lybia.

Ammonia is an invisible gas possessing a powerful, irritating odor, and intensely alkaline properties.

SUG. Try the effect of ammonia upon a strip of moist, red litmus paper.

This gas is very soluble in water, 1^{cc} of water at 0° C. absorbing 1148^{cc} of ammonia; and 1^{l} at 0° and 760^{mm} pressure weighs 0.762^{g}. It can easily be condensed to a liquid under a pressure of 7 atmospheres at + 15.5° C.; and this liquid, on being cooled to – 75° C., becomes a transparent solid.

In passing from a liquid to a gaseous state, gases always absorb a large amount of heat. M. Carré has taken advantage of this fact in constructing an ice machine. (Fig. 11.)

B is a boiler containing a strong solution of ammonia. C is a condenser with an air-tight space between its double walls, the whole being surrounded by the non-conducting covering, H. B is gradually warmed over a slow fire, while C is placed in a vessel of cold water. The ammonia of the aqueous solution in B is driven into the air-tight space in C, where it is condensed by its own pressure. Water is now placed in C, and B is subjected to a cold bath, when the liquid ammonia in the walls of C quickly evaporates, and is absorbed by the cold water in B. This evaporation abstracts so much heat from the water in C that it is soon frozen.

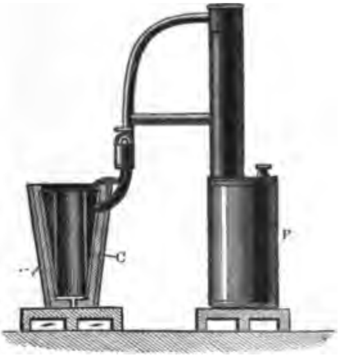

FIG. 11.

EXP. 52 P. Place in a beaker glass a dilute solution of nitric acid, HNO_3; now carefully add ammonia until the solution is neutralized so that it does not affect litmus paper. Gently evaporate this solution to dryness, when a crystalline salt is obtained.

Ammonia unites with acids to form salts, and is known as the *volatile alkali.* This action with acids may be illustrated by the equations: —

$$NH_3 + HCl \quad = NH_4Cl.$$
$$NH_3 + HNO_3 = NH_4NO_3.$$

It will be seen that the ammonia, NH_3, is added directly to the acid. The compounds thus formed are called *ammonium compounds*, the group NH_4 contained in them being known as *ammonium.*

Since ammonia neutralizes an acid, it is used in cases of accidents when acids are spilled upon the clothes or flesh. But should the acid be received in the face, it is best to wash it off quickly with much water, then with a weak solution of ammonia, and finally, without rubbing, to cover the injured parts with sweet oil.

Ammonia produces a stimulating effect upon the human system when inhaled, and is often employed in cases of fainting, or where over-doses of chloroform, laughing gas, ether, etc., have been taken. It also neutralizes the effects of such poisonous or irritating gases as chlorine, sulphur dioxide, and nitrogen tetroxide.

55. **Tests for Ammonia,** NH_3. — 1. When present in very small quantities, as in drinking-water, ammonia is best detected by means of Nessler's test solution. (See App.)

2. When present in considerable quantities, add to the solution to be tested potassium hydroxide, KOH, and warm gently. Ammonia, if present, is driven off, and may be recognized as follows: —

(*a*) By its pungent smell.

(*b*) By turning moistened red litmus paper blue.

(*c*) A warm glass rod previously moistened in hydrochloric acid, HCl, is coated white by ammonia gas. Characteristic white fumes (NH_4Cl) are also produced when much ammonia is present.

NITROGEN AND OXYGEN.

56. Nitrogen indirectly unites with oxygen to form five oxides or compounds, viz.: —

N_2O, Nitrogen Monoxide or Nitrous Oxide.
NO, (or N_2O_2) Nitrogen Dioxide or Nitric Oxide.
N_2O_3, Nitrogen Trioxide or Nitrous Anhydride.
NO_2 (or N_2O_4), Nitrogen Tetroxide.
N_2O_5, Nitrogen Pentoxide or Nitric Anhydride.

NITROGEN MONOXIDE, N_2O.

57. **Occurrence.** — This substance is a gas, and never occurs free in nature. It is often known by the common name of *nitrous oxide.*

58. **Preparation.** — EXP. 53 P. Place in a test-tube a small quantity of ammonium nitrate, NH_4NO_3, and heat gently in the Bunsen flame. Note the sweetish odor. The gas thus obtained is nitrogen monoxide. Insert a glowing match, as in testing for oxygen; also try a burning match.

QUERIES. How does this gas behave, in comparison with oxygen? How can you distinguish it from oxygen?

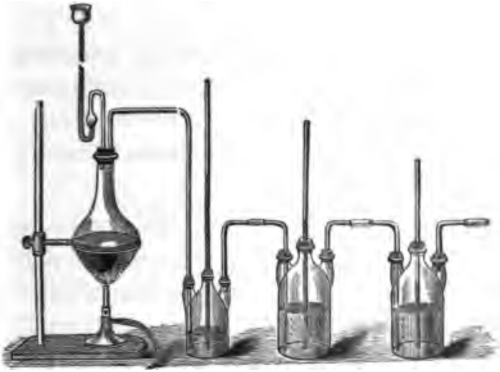

FIG. 12.

EXP. 54 T. Place 20^g ammonium nitrate, NH_4NO_3, in a generating flask, and connect with three wash-bottles, as shown in Fig. 12. The thistle-top tube contains a small quantity of mercury, and will serve as a very efficient safety-valve. A moderately strong heat will serve to decompose the contents of the flask, thus: —

$$NH_4NO_3 = N_2O + 2\,H_2O.$$

But the nitrogen monoxide may contain impurities such as nitric oxide, NO, and chlorine. It is accordingly washed through a solution of ferrous sulphate, $FeSO_4$, which is placed in the first wash-bottle, to remove the nitric oxide. The second wash-bottle contains a solution of potassium hydroxide, to remove the chlorine; while the third bottle contains water. The contents of the bottles must be warm, since nitrous oxide is somewhat soluble in cold water, and but slightly so in warm solutions. The gas thus prepared is best collected in rubber gas-bags, where it may be kept for experimental purposes in studying its properties.

Nitrogen monoxide may be prepared by other methods; but the one given above is always used in its practical preparation.

59. **Properties.** — Exp. 55 op. Inhale a small quantity of pure nitrogen monoxide, as prepared above, and note its odor, and taste.

Sug. Student, make the same experiments with nitrogen monoxide as with oxygen.

Nitrogen monoxide is a colorless gas possessing a pleasant smell and sweetish taste, and when mixed with air, and inhaled, produces a peculiar intoxication, while consciousness remains, whence it derived its name "Laughing Gas." When inhaled in a pure state, it affects the system thus: —

1. Intoxication and singing in the ears are experienced.
2. Insensibility follows.
3. If continued long enough, death ensues.

This gas is chiefly used for anæsthetic purposes, by dentists and physicians, who keep it stored under pressure in tanks or cylinders.

It is soluble in water, 100^{cc} of water at 0° dissolving 130^{cc} of nitrogen monoxide, while alcohol dissolves still greater quantities.

This gas can be liquefied at 0° by a pressure of 30 atmospheres, or at ordinary pressures by reducing its temperature to – 88° C. By mixing this liquid with carbon bisulphide, CS_2, and by placing the mixture in a receiver from which the air and vapors are afterwards rapidly exhausted, the remarkably low temperature of – 140° C. has been reached.

Nitrogen monoxide will support combustion ; but in order to initiate the process, some substances, as sulphur, must be freely burning. Ignited sodium, potassium, and phosphorus, however, burn in it quite as briskly as in oxygen.

The specific gravity of this gas is 1.527; and 1^l at 0° and 760^{mm} weighs 1.972^g.

60. Tests for Nitrogen Monoxide, N_2O. — This gas closely resembles oxygen, from which it is easily distinguished, first by its odor and taste, and second by its great solubility in cold water.

Nitrogen Dioxide, NO.

61. Preparation. — This oxide of nitrogen, also called *nitric oxide*, does not occur free in nature.

Exp. 56 p. Place copper filings in the generating-flask A; then adjust the cork with the tubes B and C, as shown in Fig. 13. Now, through the tube B, introduce into A dilute nitric acid (sp. grav., 1.2). At first A will be filled with reddish-brown fumes; but these disappear as soon as the air is expelled from the apparatus, and a colorless gas, NO, collects in G. Note the disagreeable odor. Allow some of the gas to escape into the air. What do you observe?

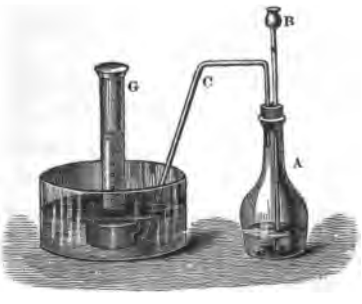

Fig. 13.

Nitrogen dioxide can be prepared from nitric acid by the action of other metals than copper, such as iron, zinc, silver, and mercury. It might be well to know, however, that this gas thus prepared contains impurities such as nitrogen and nitrogen monoxide; but these impurities are insignificant in qualitative work. The reaction with copper is expressed thus: —

$$3\,Cu + 8\,HNO_3 = 3\,Cu\,(NO_3)_2 + 4\,H_2O + 2\,NO.$$

62. Properties. — Nitrogen dioxide is a colorless gas, but when brought in contact with the air, it unites with atmospheric oxygen to form the reddish-brown fumes, NO_2, seen at the beginning of the last experiment.

Sodium, potassium, and phosphorus, when very strongly ignited, will burn in this gas, but not so readily as in nitrogen monoxide, since it does not decompose as readily as the latter gas, to supply oxygen for the purpose of combustion. What takes place when bodies burn in these oxides of nitrogen may be seen from the following equations: —

1. $N_2O + 2\,Na = Na_2O + 2\,N.$
2. $NO + 2\,K = K_2O + N.$

SUG. Try NO with a glowing match. What result?

Nitrogen dioxide was formerly considered as an incondensible gas, but it became a liquid at −11° under 104 atmospheres.

The specific gravity of this gas is 1.038; and 1^l under standard conditions weighs 1.343^g.

QUERY. At what temperature and pressure have we given the weights of the gases up to this time?

63. Tests for Nitrogen Dioxide, NO. — 1. We can distinguish this gas by the brownish-red fumes which it gives upon escaping into the air.

2. When passed into a solution of ferrous sulphate, $FeSO_4$, the solution turns brown.

NOTE. By heating this solution, chemically pure NO may be obtained.

NITROGEN TRIOXIDE, N_2O_3.

64. **Preparation.** — This gas also does not occur in nature. The following is the best method of preparing it: —

EXP. 57 P. To a few grains of starch in a test-tube add reagent nitric acid, HNO_3, and gently heat in the Bunsen flame. Dark-reddish fumes of the trioxide are given off.

EXP. 58 P. Place in a generating-flask 10^g of starch, and cover with nitric acid. Cork the flask tightly with a rubber stopper, carrying a bent delivery-tube, which projects into another flask filled with cold water and surrounded by a mixture of ice and salt. Gently heat the generating-flask containing the starch and nitric acid, when the trioxide is plentifully produced, and absorbed by the cold water with which it unites, thus: —

$$N_2O_3 + H_2O = 2\,HNO_2,$$

nitrous acid being formed by this union. Also, pass a portion of the nitrogen trioxide into a cold solution of potassium hydroxide, when potassium nitrite will be formed, thus: —

$$2\,KOH + N_2O_3 = 2\,KNO_2 + H_2O.$$

Preserve the above for work under nitrous acid.

Nitrogen trioxide is of itself unimportant, except as being the starting-point from which nitrous acid and its compounds are formed. Consequently we will again refer to it, omitting its tests, etc., for the present, since they are the same as for nitrous acid. (Art. 72.)

NITROGEN TETROXIDE, NO_2 (or N_2O_4).

65. **Preparation, etc.** — This oxide of nitrogen is unimportant, and is easily obtained by artificial processes, *e.g.*, when lead nitrate, $Pb(NO_3)_2$, is heated in a hard glass retort, dense reddish fumes of the tetroxide are evolved, thus: —

$$Pb(NO_3)_2 = PbO + 2\,NO_2 + O.$$

These fumes can be condensed by passing them into a U-tube surrounded by a freezing mixture. When passed into water, the following reaction occurs: —

$$2\,NO_2 + H_2O = HNO_2 + HNO_3.$$

NITROGEN PENTOXIDE, N_2O_5.

66. **Preparation, etc.** — Nitrogen pentoxide is a white crystalline solid assuming the form of rhombic crystals or six-sided prisms. Although from a scientific standpoint it is an important compound, being the anhydride of nitric acid (by anhydride of an acid we mean a certain oxide that, uniting with water, produces that acid), it is, nevertheless, so unstable, and difficult of preparation, that it is not advisable to attempt its production in small laboratories. There are several methods of obtaining the pentoxide, one of which is by passing dry chlorine gas through a glass tube containing silver nitrate. The reaction occurs in two stages, thus: —

1. $AgNO_3 + 2\,Cl \quad = NO_2Cl + AgCl + O.$
2. $NO_2Cl + AgNO_3 = N_2O_5 + AgCl.$

The pentoxide unites with water, thus: —

$$N_2O_5 + H_2O = 2\,HNO_3.$$

THE COMPOUNDS OF NITROGEN, OXYGEN, AND HYDROGEN; OR, THE NITROGEN ACIDS.

67. There are three acids in this series, viz.: —

1. Hyponitrous Acid (theoretical), HNO.
2. Nitrous Acid, HNO_2.
3. Nitric Acid, HNO_3.

None of these acids occur free in quantity, and only the last two have been prepared in the free state. It is interesting to note the manner in which these acids may be supposed to originate from the union of their anhydrides with water, thus: —

$$N_2O + H_2O = 2\,HNO.$$
$$N_2O_3 + H_2O = 2\,HNO_2.$$
$$N_2O_5 + H_2O = 2\,HNO_3.$$

QUERY. Can they all thus be produced?

HYPONITROUS ACID, HNO, AND HYPONITRITES.

68. **Preparation.** — Hyponitrous acid has not been isolated, but its compounds (called *hyponitrites*) with certain metals are known.

EXP. 59 P. Add sodium amalgam to a strong solution of potassium nitrate in a beaker, until hydrogen gas escapes. Potassium hyponitrite will be formed, thus: —

$$KNO_3 + 4H = KNO + 2H_2O.$$

QUERIES. Is the above solution alkaline? Whence comes the H of the above reaction?

Retain the solution thus prepared to make the following: —

69. **Tests for Hyponitrites.** — 1. Hyponitrites in alkaline solutions precipitate lead hyponitrite, $Pb(NO)_2$, upon

addition of lead acetate, $Pb(C_2H_3O_2)_2$. This precipitate is white, changing to yellow.

$$Pb(C_2H_3O_2)_2 + 2\,KNO = Pb(NO)_2 + 2\,K(C_2H_3O_2).$$

2. Hyponitrites in alkaline solutions do not turn a solution of starch paste and potassium iodide, KI, blue, while acid solutions (use acetic acid to acidulate) do effect this change.

3. In solutions acidulated with acetic acid they bleach a solution of potassium permanganate, $K_2Mn_2O_8$.

4. Upon adding silver nitrate to a nearly neutral hyponitrite solution, silver hyponitrite, AgNO, a yellow precipitate, is thrown down.

$$KNO + AgNO_3 = AgNO + KNO_3.$$

NITROUS ACID, HNO_2, AND NITRITES.

70. Preparation. — Nitrous acid is a very unstable compound; but its salts, called the nitrites, are stable and well known. It may be prepared by the action of nitrogen trioxide upon water. (Art. 64.)

QUERY. How can you obtain a nitrite?

71. Properties. — Nitrous acid, upon standing or upon being heated, undergoes decomposition, thus: —

$$3\,HNO_2 = HNO_3 + 2\,NO + H_2O.$$

The nitrites are all soluble in water; and since they are produced upon the surface of the earth by the transformations of decaying nitrogenous substances, they will be found in drinking water contaminated with sewage. (See Exp. 37.)

All nitrites deflagrate when thrown upon hot charcoal, and they are decomposed by the action of stronger acids, giving off fumes of nitrogen trioxide, N_2O_3.

Experimental Problem. *Given:* Starch, nitric acid, and potassium hydroxide. Prepare, and test as you proceed, 1st, N_2O_3; 2d, HNO_2; 3d, KNO_2; 4th, N_2O_3; using in each case the last substance produced to obtain the next succeeding compound.

72. Tests for Nitrous Acid and Nitrites. — 1. Free nitrous acid turns a solution of starch paste and potassium iodide blue.

2. It bleaches a solution of potassium permanganate.

3. In solutions acidified with acetic acid, the nitrites bleach a solution of potassium permanganate. When acidulated with acetic acid, they give a white precipitate, $AgNO_2$, with silver nitrate.

Exp. Prob. Let the student have two unlabelled solutions, one a nitrite and one a hyponitrite; then let him determine which is the nitrite.

Nitric Acid, HNO_3, and the Nitrates.

73. Occurrence and Preparation. — Free nitric acid barely occurs in nature; but its compounds, as potassium nitrate, KNO_3, or saltpetre, and sodium nitrate, $NaNO_3$, or Chili saltpetre, are found in large quantities.

Exp. 60 t. Place in the retort A (Fig. 14) equal parts, by weight, of strong sulphuric acid and pulverized potassium nitrate. Surround the receiver R with snow or ice, or allow a stream of cold water continually to flow over it. Apply heat to A, which rests upon a piece of wire gauze, when nitric acid will be given off and condensed in R. As soon as the operation is finished, pour the acid into a glass-stoppered bottle, and reserve for a few experiments which will be given under "Properties."

Nitric acid thus prepared is apt to be colored, owing to the presence of some of the lower oxides of nitrogen; but chemically pure nitric acid is colorless. The commercial acid is prepared on the large scale by treating Chili saltpetre, $NaNO_3$, in iron retorts with sulphuric acid, the vapors being condensed in stoneware condensers. The acid is afterwards purified by distillation. If much water be present, a weak acid is at first obtained; if little water be present, a stronger acid distils over; but in either case an acid of the specific gravity of 1.4 is finally obtained.

74. Properties. — Exp. 61 T. Place in an evaporating dish 2^{cc} or 3^{cc} of the strong acid obtained above. With the aid of a long-handled deflagrating spoon, drop in a small piece of phosphorus. It usually takes fire, and that, perhaps, with explosive violence. There is some danger attendant upon this experiment.

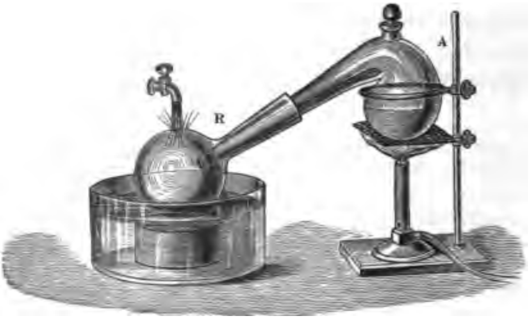

FIG. 14.

Exp. 62 P. Heat to redness some finely-powdered charcoal in an iron sand-bath. A few drops of strong nitric acid will cause the charcoal to deflagrate.

Nitric acid is an exceedingly powerful oxidizing agent owing to the ease with which it gives up a part of its oxygen. This oxygen, when in a *nascent* condition, that is, at the moment it is liberated, is by far more active chemically than when in a free condition. We may here note that the same is true of all elements when in a nascent state.

Exp. 63 p. Ignite a small quantity of spirits of turpentine in an evaporating dish by carefully adding a few drops of a mixture of equal parts nitric and sulphuric acids.

Nitro-glycerine is prepared by treating common glycerine with these acids, at low temperatures. What is dynamite?

Exp. 64 p. Sprinkle upon red-hot charcoal finely-powdered potassium nitrate. What occurs?

Common gunpowder is a mechanical mixture of potassium nitrate, sulphur, and charcoal. Gun-cotton and wood-powder are made by treating vegetable fibres with nitric acid.

Exp. 65 p. To about 20^{cc} pure water in an evaporating dish add one or two drops of nitric acid. Now drop in some goose-quill clippings or the parings of the finger-nails. Evaporate the solution to dryness, when the cuttings will turn yellow. Also try the same upon white silk thread. What occurs?

Query. How does nitric acid act upon the skin and similar organic substances?

Exp. 66 p. Drop a few drops of nitric acid upon copper filings in a test-tube, and note the brownish-red fumes evolved. What are these fumes?

When metals react with nitric acid, substances called *nitrates* are obtained, some of which are very useful, as we shall hereafter see.

Nitric acid is one of the most important acids known in chemistry. In addition to the uses above indicated, we may add that it is used in making coal-tar colors and various other economical products, while in the laboratory it is used as an indispensable reagent, serving as a solvent for most metals, — since the nitrates are all soluble in water, — and as a point of departure in the preparation of all the other oxides and acids of nitrogen.

75. **Tests for Nitric Acid, HNO_3, and the Nitrates.** — 1. Make in a test-tube a solution of ferrous sulphate, $FeSO_4$, and add sulphuric acid, H_2SO_4. Shake well, and allow to stand till cool; then, without mixing, carefully pour in the solution to be tested. Now lightly tap with the finger on the side of the test-tube. If nitric acid or a nitrate be present, a brown ring will be formed where the liquids meet. Upon shaking, the ring disappears.

EXPLANATION. Nitric oxide, NO, is liberated, which, uniting with the ferrous sulphate, forms the brown substance of the ring, thus: —

$$2\,KNO_3 + 4\,H_2SO_4 + 10\,FeSO_4 =$$
$$K_2SO_4 + 3\,Fe_2(SO_4)_3 + 4\,H_2O + \underline{2\,(FeSO_4)_2NO}.$$

2. A solution of a nitrate with sulphuric acid and a few bits of copper will give off reddish fumes.

EXPL. $2\,KNO_3 + 4\,H_2SO_4 + 3\,Cu = K_2SO_4 + 3\,CuSO_4 + 4\,H_2O + \underline{2\,NO}$. The NO coming in contact with the air absorbs atmospheric oxygen, thus: $2\,NO + 2\,O = 2\,NO_2$. What is NO_2?

3. Nitrates are distinguished from nitrites thus: Add acetic acid to ferrous sulphate, then add the solution to be tested. Nitrates produce no change: nitrites turn the solution brown.

HYDROXYLAMINE, NH_3O.

76. Nitrogen, hydrogen, and oxygen, form another compound of some scientific interest, hydroxylamine, NH_3O, which may be regarded as a compound of ammonia and

oxygen. If we represent ammonia thus, $N\left\{\begin{matrix}H\\H\\H\end{matrix}\right.$, we may represent hydroxylamine thus, $N\left\{\begin{matrix}H\\H\\OH\end{matrix}\right.$, showing that the group OH, or *hydroxyl*, which the student must have noticed as occurring in the hydroxides, has displaced one atom of hydrogen in ammonia.

This substance in an aqueous solution possesses strong reducing powers, being capable of throwing down, in a finely-divided state, some of the metals from their solutions. It is produced by the action of nascent hydrogen on nitric oxide, thus: —

$$NO + 3H = NH_3O.$$

It turns a solution of cupric sulphate orange-yellow, forming cuprous oxide, Cu_2O. This reaction serves as a test.

EXERCISES IN NITROGEN.

1. **Prob.** How many litres of air would be required in preparing 5^l of nitrogen? How much phosphorus?

2. Make a cork boat, and place thereon a small quantity of iron filings moistened with ammonium chloride; float the boat on water, and place over it a tall glass jar, the mouth of which is to dip under water; note the volume of air, and in two or three days again examine. What change has occurred in the iron? What alteration in the volume of air? How can you determine the volume of O and N in air, provided the iron has united with all the oxygen? Test the residual gas. Is it nitrogen?

3. **Prob.** How many grams of NH_3 can you obtain from 80^g of NH_4Cl?

4. **Prob.** How many grams of nitrous oxide are to be had from 400^g of NH_4NO_3?

5. **Prob.** How many pounds of nitric acid may be obtained from one ton of Chili saltpetre? How much H_2SO_4 will be required to produce it?

6. If you had KNO_3, H_2SO_4, Na, Hg, starch, and NH_4OH, and no other reagents, show how you could prepare all the oxides and acids of nitrogen excepting N_2O_5.

7. Which compound treated in this chapter is the most valuable to commerce? Which next?

8. Write a short sketch of the chemist Rutherford, who discovered nitrogen in 1772.

9. What is the derivation of the words *nitre* and *nitrogen?* (Consult a dictionary.)

10. NH_3 represents *two volumes* of ammonia. In its production, one volume of N has united with three volumes of H. How much condensation has occurred? What is the density (Art. 87) of NH_3 as compared with H? (SUG. $14 + 3 = 17$ and $17 \div 2 = 8.5$.) What is the density of N_2O? Of N_2O_3?

11. In practice one determines the *amount* of ammonia present in drinking-water, thus: Proceed as in Exp. 35, using 1^l of the water to be tested. The first jar contains three-fourths of all the ammonia in the sample (Wanklyn). In a similar tall jar is placed 50^{cc} *pure* water and about 4^{cc} Nessler's solution. To this, from a burette graduated to tenths of a cubic centimetre, is added a standard solution of ammonium chloride, NH_4Cl, drop by drop, with constant stirring until the same color is reached as in the first jar (Exp. 35). The number of cubic centimetres standard solution added equals the number of milligrams of ammonia per litre.

The standard solution of ammonium chloride is prepared by dissolving 3.15^g of the dry salt in 1^l distilled water. See App., Art. 78.

Good drinking-water should not contain over 0.08 parts per 1,000,000, of free ammonia.

QUERY. Should the qualitative tests fail to detect organic matter, ammonia, nitrites, etc., can there be a question as to the potableness of the water under examination?

12. Nitric acid containing oxides of nitrogen may be freed from the latter by passing through it for some time a current of pure air.

GENERAL NOTE. Recent investigations throw doubt upon the existence of free nitrogen trioxide in a gaseous condition. Some authors also give ammonium hydroxide, NH_4OH; but there are grave doubts as to its existence. It is, at least, decomposed by boiling.

CHAPTER IV.

BINARY COMPOUNDS. — ACIDS. — BASES. — SALTS. — CHEMICAL NOMENCLATURE.

77. **Binary Compounds** are those which consist of but two elements. Oxygen unites with all other elements except fluorine, and the compounds thus formed are known as *oxides*. Similarly, the binary compounds of sulphur are known as *sulphides;* those of chlorine, bromine, and iodine, as *chlorides*, *bromides*, and *iodides*.

The principal elements whose binary compounds are named in this way are bromine, chlorine, fluorine, iodine, oxygen, selenium, sulphur, and tellurium.

To distinguish between the different oxides, chlorides, etc., the name of the element in combination with oxygen, chlorine, etc., is prefixed. Thus *sodium chloride* is the compound of sodium and chlorine; *magnesium chloride* is the compound of magnesium and chlorine; *barium oxide* is the compound of barium and oxygen; *potassium iodide*, the compound of potassium and iodine, etc.

Sug. Student, name the compounds, the formulae of which are here given: — CaO, $BaCl_2$, KF, NaI, MgO.

It sometimes occurs that oxygen, chlorine, bromine, etc., unite with other elements in more than one proportion, as illustrated by the formulae, HgO and Hg_2O, CuO and Cu_2O, $FeCl_2$ and Fe_2Cl_6, etc. In these cases the simple prefixing of the name of the element which is in combination with oxygen, chlorine, etc., will not suffice. Hence the name is modified by the suffixes *-ic* and *-ous*. We have not simply mercury compounds, but *mercuric* and *mercurous* compounds, etc. That compound which contains the smaller proportion of oxygen, chlorine, etc., is designated by the suffix *-ous*, and that which contains the larger proportion is designated by the suffix *-ic*. Thus, of the two compounds of mercury and oxygen, that which has the formula Hg_2O is called *mercurous oxide*, because it contains less oxygen in proportion to the mercury than the other compound, HgO. The latter is called *mercuric oxide*. In naming compounds of copper, iron, tin, lead, and some other elements, when the syllables *-ic* and *-ous* are necessary, the Latin names of the elements are used. Instead of speaking of copperous and copperic, or of ironous and ironic compounds, we use the words *cuprous* and *cupric*, *ferrous* and *ferric*, compounds, etc. The compounds CuO and Cu_2O are known respectively as *cupric* and *cuprous oxides*: $FeCl_2$ and Fe_2Cl_6 are called *ferrous* and *ferric chlorides*.

There are cases in which a given element unites with oxygen, chlorine, etc., in more than two proportions. It is then necessary to use other methods in naming the compounds. Manganese forms four compounds with oxygen. These have respectively the compositions expressed by the formulas MnO, Mn_2O_3, Mn_3O_4, and MnO_2. To these are sometimes given the names *manganous oxide*, MnO; *manganic oxide*, Mn_2O_3; *manganoso-manganic oxide*, Mn_3O_4, the name signifying that the compound is made up of manganous and manganic oxides; and *manganese dioxide*, MnO_2.

It is not uncommon to indicate by the name the number of oxygen atoms represented in the formula, as in the case of oxides.

Those containing *one* atom of oxygen are called ***monoxides;***
" *two* atoms " " ***dioxides;***
" *three* " " " ***trioxides;***
" *four* " " " ***tetroxides;***
" *five* " " " ***pentoxides***, etc.

The relation 2 to 3 is sometimes expressed by the word "sesqui," *e.g.*, Fe_2O_3, *sesquioxide of iron*, which is the old name for what is now called *ferric oxide.*

78. **Acids.** — Among the compounds thus far considered are nitric and nitrous acids; and frequent reference has been made to sulphuric acid and hydrochloric acid. Indeed, it would be difficult to write a page on any chemical subject without the use of the word "acid." What is an acid? An exact definition cannot well be given. By the term "acid" we mean a body with certain physical and chemical properties, the chief of which are the following: a sour taste; the power to turn certain vegetable colors, as to turn blue litmus red; the power of giving up hydrogen, and taking up metals (bases) in its place.

Exp. 67 p. Student, test with blue litmus every acid to be found in the laboratory. Do all the acids have the same effect on the color? In testing, take a few drops of the acid in a test-tube half full of water. Try substances which are not acids, as common salt. What effect is produced?

According to the above statement regarding the properties of acids, all acids must contain hydrogen. It does not follow that all bodies which contain hydrogen are acids. Ammonia, NH_3, for example, has properties quite the opposite of those possessed by acids; and many other examples might be cited. In order to have acid properties, we must have the hydrogen in combination with certain elements, or groups of elements.

The elements whose hydrogen compounds are markedly acid are chlorine, bromine, iodine, and fluorine, which give hydrochloric acid, HCl; hydrobromic acid, HBr; hydriodic acid, HI; and hydrofluoric acid, HF. The hydrogen compounds of sulphur, selenium, and tellurium, are weak acids.

Most acids consist of hydrogen in combination with oxygen and some other element, as nitric acid, HNO_3; nitrous acid, HNO_2; sulphuric acid, H_2SO_4, etc. They are commonly called *oxygen acids* to distinguish them from those which contain no oxygen. There are a great many acids belonging to this class, but only a few of them are in common use.

In naming the oxygen acids, the same suffixes *-ous* and *-ic* are used, as in the case of binary compounds, and with the same significance.

If an element forms only one acid with oxygen and hydrogen, the suffix *-ic* is used. If it forms two acids, that which contains the smaller proportion of oxygen is designated by the suffix *-ous*, and that which contains the larger proportion of oxygen, by the suffix *-ic*. Thus we have

Nitrous acid, HNO_2,
and Nitric acid, HNO_3;

Sulphurous acid, H_2SO_3,
and Sulphuric acid, H_2SO_4, etc.

In those cases in which more than two acids are formed by the same elements, prefixes are used in addition to the suffixes. A good illustration of the use of these prefixes is furnished by the acids of chlorine. This element forms four acids with oxygen and hydrogen. They are represented by the formulae $HClO$, $HClO_2$, $HClO_3$, and $HClO_4$. Of these the second and third are known as *chlorous* and *chloric* acids. The first is called *hypochlorous* acid, which signifies that it is below chlorous acid as regards the amount of oxygen it contains. The fourth is called *perchloric* acid, which signifies that it is beyond chloric acid in the series. These prefixes *hypo-* and *per-* are frequently used in this sense.

79. **Bases.** — There are certain compounds which have properties almost exactly the opposite of those of acids. They are called *bases*. The name "base" has been applied to various bodies, and with different meanings. In general, we mean by a *base* a substance which has the power of neutralizing acids, that is, destroying their acid properties. The bases, like the acids, consist of certain elements in combination with oxygen and hydrogen. Some elements unite with oxygen and hydrogen to form acids; and others unite with oxygen and hydrogen to form bases. Nearly all the compounds which the metals form with hydrogen and oxygen are bases. Examples are: potassium hydroxide, KOH; calcium hydroxide, $Ca(OH)_2$, etc. The stronger bases are known as *alkalies*, among which are the hydroxides of potassium and sodium, formerly called *caustic potash* and *caustic soda.*

80. **Salts.** — When an acid and a base react, they tend to *neutralize* each other. The acid properties and the basic properties are usually both destroyed, and a new body is formed which is neither acid nor base. This new body is called a *salt.* The relation between an acid and the salts derived from it will readily be seen by examining the following formulae: —

$$\text{Hydrochloric acid, HCl, yields the salts} \begin{cases} \text{NaCl,} \\ \text{KCl,} \\ \text{CaCl}_2\text{, etc.} \end{cases}$$

Nitric acid, HNO_3, yields the salts . $\left\{\begin{array}{l} KNO_3, \\ NaNO_3, \\ Ba(NO_3)_2, \text{ etc.} \end{array}\right.$

Sulphuric acid, H_2SO_4, yields the salts $\left\{\begin{array}{l} K_2SO_4, \\ BaSO_4, \\ Na_2SO_4, \text{ etc.} \end{array}\right.$

On comparing the salts with the acid from which they are derived, we see that the difference between them is simply this, that the acid contains hydrogen while the salts contain something in the place of the hydrogen. We shall see later that this something which takes the place of hydrogen is called a *metal*. Thus, in the examples given above, the metals sodium, Na, potassium, K, calcium, Ca, and barium, Ba, take the place of hydrogen in the acids.

Each acid can yield at least one salt with every metal, and in some cases more than one. The salts of each acid receive a general name, and we distinguish between the different salts of the same acid by prefixing the name of the metal.

The salts of the simplest acids, such as hydrochloric, hydrobromic, and hydriodic acids, are named, as described above, under the head "Binary Compounds" (see p. 73).

Salts of the oxygen acids are named thus: when the name of the acid ends in *ic*, the name of its salts ends in *ate;* and, when the name of the acid ends in *ous*, the name of its salts ends in *ite*. Thus, a salt of *nitric* acid is called a *nitrate;* of *nitrous* acid, a *nitrite;* of *sulphuric* acid, a *sulphate;* of *sulphurous* acid, a *sulphite*, etc. From nitric acid we thus have a series of nitrates corresponding to the different metals. We distinguish between them by using the names of the metals as adjectives, as in the case of binary compounds. The potassium, sodium, and calcium salts of nitric acid, for example, are called ***potassium nitrate***, KNO_3, ***sodium nitrate***, $NaNO_3$, and ***calcium nitrate***, $Ca(NO_3)_2$.

The metals mercury, iron, copper, and some others yield two different classes of salts, corresponding to the lower and higher oxides already mentioned. Just as we have mercurous and mercuric oxides and chlorides, ferrous and ferric chlorides, etc., so also we have mercurous and mercuric nitrates, sulphates, etc., and ferrous and ferric nitrates, sulphates, etc. The two nitrates of mercury will serve as examples. We have

Mercurous nitrate, $Hg_2(NO_3)_2$,
and Mercuric nitrate, $Hg(NO_3)_2$.

The principle of nomenclature adopted for these salts is the same as that described in connection with the oxides, chlorides, etc. The name of that salt which contains the smaller proportion of the acid constituent ends in *ous*, while the name of that one which contains the larger proportion of the acid constituent ends in *ic*.

The action of metals upon acids may be illustrated by the following equations: —

$$Zn + H_2SO_4 = ZnSO_4 + 2\,H;$$
$$Zn + 2\,HCl = ZnCl_2 + 2\,H.$$

In these cases the metal simply replaces the hydrogen which is set free. This action takes place only in the case of the stronger acids.

When an acid acts upon a base, the action is as represented below: —

$$KOH + HNO_3 = KNO_3 + H_2O;$$
$$NaOH + HNO_3 = NaNO_3 + H_2O;$$
$$2\,KOH + H_2SO_4 = K_2SO_4 + 2\,H_2O;$$
$$Ca(OH)_2 + H_2SO_4 = CaSO_4 + 2\,H_2O.$$

This kind of action takes place between all acids and all bases.

81. Acid and Normal Salts. — The simplest acids, such as hydrochloric and nitric acids, yield only one salt each with most of the metals. Thus hydrochloric acid and potassium yield only one potassium chloride, KCl, which is a neutral body; nitric acid and sodium yield only one sodium nitrate, $NaNO_3$, which is also neutral.

There are some acids, like sulphuric acid, H_2SO_4, which have the power of yielding two or more salts with the same metal. Thus sulphuric acid yields with potassium not only the salt, K_2SO_4, potassium sulphate, but another salt, of the formula $KHSO_4$, which contains only half as much potassium as the first. In the first case all the hydrogen of the acid has been replaced, and the resulting compound has no acid properties. It is a *normal salt.* In the second case a part of the hydrogen is left, and the compound still has acid properties. It is both acid and salt, and is called an *acid salt.*

A *normal salt* is one which is formed by replacing all the hydrogen of an acid with a metal.

An *acid salt* is one which is formed by replacing only a part of the hydrogen of an acid with a metal.

In naming the acid salts it is customary to indicate the number of atoms of the metal which are represented in the formula. Thus the salt $KHSO_4$ is called *mono-potassium sulphate;* the salt Na_2HPO_4 is called *disodium phosphate.* Sometimes they are referred to as acid salts, mono-potassium sulphate being called *acid potassium sulphate.*

Applications of these principles of nomenclature will be met with when the salts are considered. Meanwhile the student should familiarize himself with the main points by means of examples furnished by the teacher. A few examples are here given.

Student, name the compounds, the formulae of which are given below: —

Cu_2Cl_2, KNO_3, $Ca(NO_3)_2$, $Fe(NO_3)_2$, HgO, $NaHSO_4$,
$CuCl_2$, $NaNO_2$, $Ba(NO_3)_2$, $Fe_2(NO_3)_6$, Hg_2O, K_2SO_4.

WRITING EQUATIONS.

It is important to know how to write chemical equations, and thus avoid the necessity of committing them to memory. In the first place *we know* what substances we put together or experiment upon, and these are placed in the first member, and connected by the sign +. The substances formed are determined by experiment, or, when our knowledge is sufficient, by analogy or by induction. They are then placed in the second member, and connected by the + sign. It now remains *to balance* the equation. The fundamental principle to be remembered here is, that "matter is indestructible"; that is, *just as many atoms of a given element as appear in one member, just so many must also appear in the other.* Let us, for example, write the equations for the reaction of NaCl and H_2SO_4: we first write $NaCl + H_2SO_4 = \cdots$; by experiment, we know that under certain conditions (Art. 94) HCl and $HNaSO_4$ are formed, and we proceed to the next step, thus: $NaCl + H_2SO_4 = HNaSO_4 + HCl$. By inspection, we see that the equation *balances* and is complete. But let us suppose that the conditions are different, and that Na_2SO_4 and HCl are produced; the second step gives us $NaCl + H_2SO_4 = Na_2SO_4 + HCl$. By inspection we here see that the equation is not true, since two atoms of Na appear in the second member, and but one in the first; also one atom of H in the second, and two in the first. We may obtain the required amount of Na by doubling the NaCl; and, when this is done, the necessity for doubling the HCl becomes apparent, and the equation balances, thus: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$

Water, which is almost always present, must sometimes be taken into consideration. The equations previously given will afford good practice, also those to follow, especially those relating to the metals. Before we reach that point, however, molecular equations will be explained.

CHAPTER V.

THE ATMOSPHERE. — LAWS OF PRESSURE, TEMPERATURE, DENSITY, AND VOLUMES OF GASES. — PROBLEMS.

THE ATMOSPHERE.

82. The earth is everywhere surrounded by an ocean of gaseous vapor, called the *atmosphere*, which varies from fifty to one hundred miles in height. This variation at any one point is never ceasing, for just as in the oceans of water, so in this ocean of air, do huge waves continually surge to and fro, — waves so vast that their altitudes are measured in miles.

Every object upon the surface of the earth is subjected to the pressure exerted by the weight of air above. This pressure varies constantly, and, owing to the great mobility of the particles of air, it is exerted in all directions, — downwards, upwards, and sidewise.

This pressure is measured by an instrument called a *barometer* (Fig. 15). A is a glass tube about 800^{mm} long, sealed at the upper end, open at the lower, and provided with a scale. This tube is filled with mercury, and inverted in a cup of mercury, C. Now, since the tube itself sustains the pressure which the atmosphere would exert on this column of mercury within the

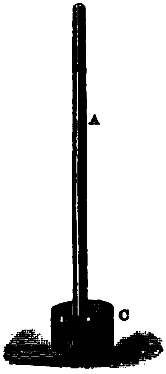

FIG. 15.

tube, in every direction except upwards, it follows that the column will remain at a higher altitude than the level of the mercury in the cup. The height of this column of mercury will depend upon how hard the atmosphere presses it upward.

At the level of the sea, in the latitude of Paris, and at 0° C., the average height of this column is 760^{mm}; hence 760^{mm} is taken as the standard pressure of the air.

As you ascend from the sea-level the column falls (why?), and as you descend it rises (why?).

As the density (Art. 88) of the mercury and the atmosphere varies, owing to changes of temperature, the height of the barometer varies; hence the necessity of taking a standard temperature, which is 0° C.

83. Measurement of the Temperature of the Atmosphere. — This is accomplished by means of instruments called *thermometers.* There are three scales in use, — Centigrade, Fahrenheit, and Reaumur (Fig. 16). Thermometers are made by blowing bulbs on capillary tubes. The bulbs and tubes are filled with mercury, and then heated till the mercury issues in vapor, when the ends are suddenly sealed by the blow-pipe flame. They are graduated by first plunging them into melting ice, the height of the column of mercury being marked 0° C., 0° R., or 32° F. The instruments are next placed in the steam of boiling water, and the height of the column of mercury marked 100° C., 80° R., or 212° F. The distances between these points are

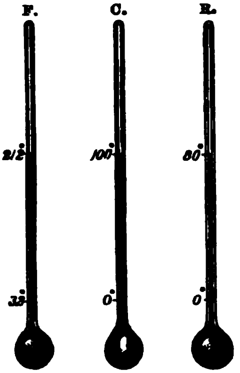

FIG. 16.

then divided into spaces (or degrees), there being 100 divisions C., 80 R., or 180 F.; divisions of the same length are also made above and below these points. From the manner of laying off these scales, it follows that

$$5° \text{ C.} = 4° \text{ R.} = 9° \text{ F.}$$

The following formulae will assist in changing from the reading of one scale to another: —

$$(a)\ \text{C.} = (\text{F.} - 32)\tfrac{5}{9}.$$
$$(b)\ \text{F.} = \tfrac{9}{5}\text{C.} + 32.$$
$$(c)\ \text{R.} = \tfrac{4}{5}\text{C.}$$

PROB. Change 98° C. to F.; 87° R. to F.; 91° F. to R.; − 18° C. to F.; − 40° F. to C.

SUG. It would be advisable for the student to learn the points of a good thermometer from his text-book in physics, and to review the metric system in his arithmetic.

NOTE. The centigrade thermometer and the metric system of weights and measurements are used throughout this work, as they best answer its purposes, and are the ones used by scientists in general.

84. Impurities in the Atmosphere. — As we have already learned, air is a mechanical mixture of nitrogen and oxygen. By this we mean pure air. But atmospheric air is never pure. It contains, —

(*a*) Moisture, as invisible vapors, clouds, and fogs. These, being lighter than the atmosphere, cause a lower barometer, especially when they are present in large quantities.

(*b*) Carbon dioxide, CO_2, produced by combustion, by the respiration of all air-breathing animals, and by the decomposition of animal and vegetable tissues.

(*c*) Ammonia (Art. 51).

(*d*) Ozone (Art. 30), or other substances having marked oxidizing power.

(*e*) Dust and smoke.

(*f*) Other gases in small quantities, which are liberated in various ways.

85. Determination of the Volumes of Nitrogen and Oxygen in the Atmosphere. — This determination is made by means of Ure's eudiometer. A measured quantity of pure air is introduced into the graduated limb, and then a volume of hydrogen, more than sufficient to combine with the oxygen of the air, is added. The whole volume is now carefully noted, the spark passed, and the diminution of volume carefully ascertained.

One-third of this diminution equals the volume of the oxygen contained in the air.

The volume of oxygen is subtracted from the volume of air introduced at the beginning, and this gives the volume of the nitrogen.

In this way we learn that the air consists of oxygen 21 volumes, and nitrogen 79 volumes, in 100 parts. These proportions vary but slightly in any locality or season.

QUERIES. What chemical action takes place when the spark is passed? How do you know one-third of the volume of diminution to be the volume of O? Through what substances would you pass air to remove its impurities?

86. Effect of Pressure on the Volume of a Gas. — If a mass of gas be confined in an air-tight cylinder, and a perfectly-fitted piston be pressed down into the cylinder, the gas will be compressed into a smaller volume.

The law for the volume of a gas under such conditions is: —

LAW I. *The volume of any gas, its temperature remaining constant, varies inversely as the pressure.*

We mean by this that volume 1 under pressure 1 becomes volume $\frac{1}{2}$ under pressure 2, volume $\frac{1}{3}$ under pressure 3, or volume $\frac{1}{4}$ under pressure 4, etc.; and the reverse of this is also true when the temperature remains the same in both cases. (How could this law be discovered if it were unknown?)

NOTE. On 1^{qcm}, at the standard pressure of 760^{mm}, the atmosphere exerts a pressure of 1033.3^{g} (nearly 15 lbs. per sq. in.), which is called a pressure of 1 atmosphere. A pressure of 2 atmospheres is 2×1033.3^{g}, etc. Now, since gases are subject to the pressure of the atmosphere, their volume varies with every change of the barometer.

SUG. The student should consult some work on physics for the experimental demonstration of the above law, as well as for that of the succeeding law, since we use them as an application of physics to chemistry.

PROBLEMS. 1. What volume will 10^{l} of gas at 762^{mm} occupy when the barometer stands at 758^{mm}?

SOLUTION. Since the volume varies *inversely* as the pressure, we have the proportion,

$$758 : 762 :: 10 : x = 10.0527 + \text{ litres. } \textit{Ans.}$$

2. 190^{cc} of gas at 760^{mm} pressure becomes how many cubic centimetres at 765^{mm}?

3. A mass of gas, 100^{l} under 755^{mm}, is subjected to a pressure of 4.5 atmospheres; what volume will it occupy? *Ans.* 22.076+ litres.

NOTE. In these problems the temperature is considered constant.

87. Effect of Heat on the Volume of Gases.—It has been found by experiment that 273 volumes of any gas at 0° become 274 volumes when its temperature is raised 1°, 275 when raised 2°, etc., increasing one volume for each degree of increase in its temperature; also that 273 volumes at 0° become 272 volumes when its temperature is lowered 1°, 271 volumes when lowered 2°, 270 when lowered 3°, etc., decreasing one volume for each degree of decrease in its temperature. According to this, the volume of a gas at $-273°$ C. would be 0; and this point is designated as the absolute 0 of temperature. Hence the absolute temperature of any body is the temperature above the ordinary $0 + 273$, or $t + 273$. Taking these ideas into account, we have: —

Law II. *The volume of any gas, its pressure remaining constant, varies as its absolute temperature, i.e, in the ratio of* $273 + t$ *to* $273 + t'$.

Rem. 1. t is the observed temperature of the gas, and t' the required temperature.

Rem. 2. Since any gas surrounded by the atmosphere will usually be of the same temperature as the atmosphere itself, it follows that the volume of that gas will vary as the thermometer varies.

Problems. 1. At $+15°$ the volume of a gas is 84^1; what will be its volume at $+85°$?

Solution. $273 + 15 : 273 + 85 :: 84 : x = 104.4166+$ litres. *Ans.*

2. A gas at $-15°$ has a volume of 18^1; what will be its volume at $100°$?

Solution. $273 - 15 : 273 + 100 :: 18 : x = 26\frac{1}{43}$ litres. *Ans.*

3. 98^1 of gas at $-4°$ become how many at $-24°$?
4. 176^1 of gas at $+100°$ become how many at $-140°$?
5. 80^1 of gas at $0°$ become how many at $-18°$?
6. 144^1 of gas at $-15°$ become how many at $0°$?

Note. In these problems the pressure is considered constant.

Problems in which both pressure and temperature vary: —

1. A mass of gas at $+15°$ and 762^{mm} pressure occupies 94^1; what will be its volume at $+25°$ and 758^{mm} pressure?

Solution. We here have a combination of the principles of Arts. 86 and 87, pressure and temperature both affecting the volume of the 94^1 in question. We will consider them separately; hence the compound proportion: —

$$\left\{\begin{array}{ll}(1)\ \text{Temperature}, & 273+15:273+25\\ (2)\ \text{Pressure}\ \ .\ \ .\ \ . & 758:762\end{array}\right\} :: 94 : x = 97.7771^{l}+. \quad \textit{Ans.}$$

2. 90^{cc} of gas at 0° and 760^{mm} occupy what volume at $-140°$ and 40 atmospheres? *Ans.* 1.09+ cubic centimetre.

NOTE. From this the student may judge of the effect of pressure and reduction of temperature.

3. 72^{l} at $-12°$ and 4 atmospheres pressure become how many litres at 100° and 760^{mm}?

4. In the evening a quantity of oxygen gas was generated in a laboratory. The oxygen receiver, holding 112^{l}, was filled while the barometer read 760^{mm} and the thermometer $+15°$ C. The next morning the barometer fell to 758^{mm}, and the janitor allowed the temperature of the room to reach $+40°$. At 4 P.M. that day the barometer read 760^{mm} and the thermometer $+18°$, when the master ascertained that he had but 94^{l} of the gas remaining; upon which he charged a student, who alone had access to the laboratory, with having used some of the oxygen. Allowing half a litre to have been absorbed by the water during the night, the temperature and pressure remaining constant meanwhile, how much gas, measured at $+15°$ and 760^{mm}, was lost owing to the fall of the barometer and negligence of the janitor? Was the master justifiable in making the charge against the student? How much (if any) of the oxygen did the student use?

88. Relation of Weight to Density. — By the density of a substance we mean the amount of that substance contained in a given volume. We have seen how the volume of a gas varies under differences of pressure and of temperature. Now, it is evident that its density varies also; *i.e.*, whatever tends to make the volume less makes the density greater, and whatever tends to make the volume greater makes the density less. Again: it is evident that the denser a given amount of gas, the greater will be its weight, and the less dense the gas, the less its weight; or, —

The weight of a given volume of gas varies directly as its density.

PROBLEMS. 1. How much will 10^{l} of oxygen weigh at $+15°$ and 765^{mm}?

SOLUTION. We know that 1^{l} of oxygen at 0° and 760^{mm} weighs 1.430^{g}; therefore we will find how many litres this gas will be at 0° and 760^{mm}, as in Art. 87, and then multiply that result by 1.430, thus: —

$$\left\{\begin{matrix} 288 : 273 \\ 760 : 765 \end{matrix}\right\} :: 10 : x = 9.5415^{l}; \text{ and } 9.5415 \times 1.430 = 13.644^{g}. \textit{ Ans.}$$

2. How much will 20^{l} of hydrogen weigh at 755^{mm} and $+20°$?

3. How much will 15^{l} of nitrogen weigh at $-112°$ and 29 atmospheres pressure?

89. Useful Problems. — I. *To find the percentage composition of a compound.* We will explain this by solving a problem: What per cent of N and H in NH_3?

SOLUTION.

$N = 14$
$3H = 3$
$NH_3 = 17$

Now, it is evident that $\frac{3}{17}$ of NH_3 is hydrogen, and $\frac{14}{17}$ is nitrogen. $\frac{3}{17}$ expressed in the form of per cent equals $300 \div 17 = 17.65\ \%$ of H. One can also readily understand that $100\ \% - 17.65\ \% = 82.35\ \%$ of N.

These percentages are valuable in that they enable us to make computations more rapidly. For example, if we wish to know how much hydrogen there is in 10^{g} of ammonia, we have simply to multiply 10^{g} by the per cent of hydrogen, and divide the result by 100, when we have the weight of the hydrogen in grams, thus: —

$$(17.65 \times 10) \div 100 = 1.765^{g}.$$

1. What per cent of oxygen in HgO? $KClO_3$?

2. What per cent of chlorine in $NaCl$? Of sodium?

II. *To find what volume will be occupied by a gas obtained from a certain weight of chemicals.* We can also best understand this by a problem: How many litres of oxygen can be obtained from 10^g of potassium chlorate, $KClO_3$, when the barometer reads 750^{mm} and the thermometer 25°?

SOLUTION. We will first ascertain what weight of oxygen 10^g of $KClO_3$ will yield. We can best do this by multiplying 10 by the per cent of O in $KClO_3$. Thus we find the weight of oxygen to be 3.918^g. We will now ascertain how many litres 3.918^g of oxygen will occupy at 760^{mm} and 0°. One litre of oxygen under these conditions weighs 1.430^g; hence, $3.918 \div 1.430 = 2.7398^l$, or the number of litres at 0° and 760^{mm}. We can now finish the problem by Arts. 86 and 87, thus:—

$$\left\{\begin{matrix} 750 : 760 \\ 273 : 298 \end{matrix}\right\} :: 2.7398 : x = 3.0305^l.$$

1. How many litres of oxygen gas may be had from 100^g HgO when the barometer stands at 755^{mm}, the thermometer reading 20°?

SUG. HgO (heated) = Hg + O.

2. How many litres of oxygen gas may be had from 500^g MnO_2, at 20° and 4 atmospheres pressure?

SUG. $3\,MnO_2$ (heated) = $Mn_3O_4 + 2\,O$.

3. How many litres of nitrous oxide may be obtained from 1^k of NH_4NO_3 when the barometer reads 750^{mm} and the thermometer +22°?

SUG. See Nitrogen Monoxide.

III. *To find the weight of chemicals required to yield a certain volume of gas.* Let us again have recourse to a problem: How many grams of $KClO_3$ will be required to fill with oxygen a receiver of 32^l capacity at 20° and 750^{mm}?

Solution. We will first find what volume 32^l of oxygen at 20° and 750^{mm} would become when reduced to 0° and 760^{mm}, in order to find the required weight of the oxygen, thus: —

$$\left\{\begin{matrix} 293 : 273 \\ 760 : 750 \end{matrix}\right\} :: 32 : x = 29.423^l.$$

Now, $29.423 \times 1.430 = 42.074^g$, or the required weight of oxygen. We may now obtain the desired weight of the potassium chlorate by dividing the weight of the oxygen by the percentage of O in $KClO_3$, or by the proportion:

$$48 : 42.074 :: 122.5 : x.$$

1. How many grams $KClO_3$ will be required to yield 20^l of oxygen at − 20° and 760^{mm}?

2. How many grams of zinc and sulphuric acid are needed to yield 40^l of hydrogen at + 24° and 765^{mm}?

Sug. $Zn + H_2SO_4 = ZnSO_4 + 2\,H$.

3. What weights of CaO and NH_4Cl are required to make 25^l of NH_3 at 15° and 749^{mm}?

Sug. $CaO + 2\,NH_4Cl = CaCl_2 + H_2O + 2\,NH_3$.

EXERCISES.

1. The following equations may be of service in making calculations upon gases: —

$$(1)\ \frac{VH}{273 + t} = \frac{V'H'}{273 + t'}.$$

V, H, and t represent respectively the volume, height of barometer, and temperature of a gas under observed conditions, while V', H', and t' represent the same under required conditions, one of which will be unknown. When $t = t'$ we have,

$$(2)\ VH = V'H' \text{ (Art. 86).}$$

When $H = H'$ we have,

$$(3)\ \frac{V}{273 + t} = \frac{V'}{273 + t'} \text{ (Art. 87).}$$

2. Make a table showing the relations between the acids and their salts.

CHAPTER VI.

CHLORINE. — ITS OCCURRENCE, ETC. — HYDROCHLORIC ACID. — AQUA REGIA. — CHLORINE OXIDES. — CHLORINE OXACIDS.

CHLORINE.

SYMBOL Cl'. — ATOMIC WEIGHT, 35.5; SPECIFIC GRAVITY, 2.450.

90. **Occurrence.** — Chlorine does not occur free in nature, owing to its great chemical activity; in combination with certain metals, however, it occurs in large quantities, as in sodium chloride, $NaCl$, or common salt. Silver chloride, $AgCl$, potassium chloride, KCl, calcium chloride, $CaCl_2$, and magnesium chloride, $MgCl_2$, occur in smaller quantities.

91. **Preparation.** — EXP. 68 P. In a test-tube place a small quantity of manganese dioxide, MnO_2, and add hydrochloric acid, HCl. Upon gently warming, chlorine is evolved as a heavy, yellowish, suffocating gas, thus: —

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + 2\,Cl.$$

Hold in the escaping gas strips of moistened litmus paper and calico printed in organic colors; they will be bleached. Also note the fumes.

This method is sometimes employed in making chlorine gas for the manufacture of bleaching-powder. (Art. 349.)

EXP. 69 P. Drop three or four small crystals of potassium chlorate into a test-tube, and add hydrochloric acid. Warm gently, and, when the chlorine fumes begin freely to appear, immediately add 3^{cm} or 4^{cm} of cold water. What occurs may be indicated thus: —

$$4\,HCl + 2\,KClO_3 = 2\,KCl + 2\,H_2O + Cl_2O_4 + 2\,Cl.$$

Try the effect of this solution upon vegetable colors as before. Also add a few drops of the solution to tinctures of litmus, carmine, and indigo; they will be bleached.

The above method is one often employed by the chemist in preparing chlorine water for such purposes as testing iodine and bromine. Hereafter the student will find frequent use for chlorine water thus prepared. It might be well to say that the Cl_2O_4 and KCl are in no wise detrimental to the solution.

Another method of preparing chlorine in the manufacture of bleaching-powder is of interest, since it is continuous and quite inexpensive. Hydrochloric acid gas, mixed with air, is passed over heated cupric sulphate, $CuSO_4$; the cupric sulphate undergoes no change, while the oxygen of the air and the hydrochloric acid react, thus: —

$$2\,HCl + O = H_2O + 2\,Cl.$$

Another and common method of preparing chlorine is as follows: —

Exp. 70 T. In the generating-flask A (Fig. 17) place equal weight of common salt, NaCl, and manganese dioxide, MnO_2, which have been thoroughly pulverized and mixed. Then add to this mixture twice its weight of dilute sulphuric acid (consisting of equal weights of water and acid). Apply a gentle heat, and chlorine gas is plentifully given off. The Woulff bottle B (Fig. 17) contains a little warm water to absorb any hydrochloric acid gas that may be produced, while C contains strong sulphuric acid to dry the gas. The thistle-top tube contains a little sulphuric acid. Collect the chlorine in tall jars. This may be accomplished by delivering the gas by means of a long glass tube extending to the bottom of the upright jar. The air will be pushed up and out of the jar.

Note. This method of collecting a gas is called *displacement*, and is employed with those gases heavier than air.

If a pure, aqueous solution of chlorine be desired, it may be obtained by attaching two or three Woulff bottles, nearly filled with cold water, and surrounded with a cooling or freezing mixture. Should the temperature of any bottle contained in the series nearly reach 0°, a crystalline hydrate of chlorine is formed, whose composition is $Cl + 5H_2O$. In thus preparing chlorine we may represent the reaction by, —

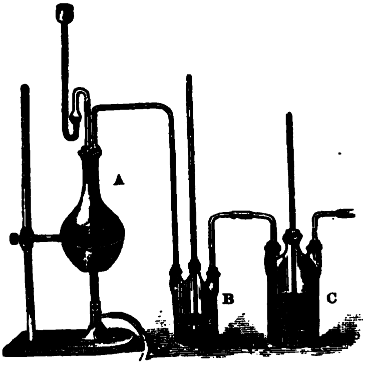

Fig. 17.

$$2NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + 2Cl.$$

In reality, however, two distinct processes are involved. In the first place the sulphuric acid, H_2SO_4, acts upon the sodium chloride, $NaCl$, giving hydrochloric acid, HCl, and mono-sodium sulphate, $NaHSO_4$. Then the manganese dioxide, MnO_2, acts upon the hydrochloric acid, HCl, giving manganous chloride, $MnCl_2$, free chlorine, and water, H_2O. If an excess of sulphuric acid is present, it decomposes the manganous chloride, $MnCl_2$, giving manganous sulphate, $MnSO_4$, and hydrochloric acid; and the latter again acts upon manganese dioxide, yielding chlorine.

The equations which give the best insight into the reactions are the following: —

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl,$$

and $$4\,HCl + MnO_2 = MnCl_2 + 2\,H_2O + 2\,Cl.$$

Manganese dioxide readily gives up one part of its oxygen, and it is this which, uniting with the hydrogen of hydrochloric acid, sets the chlorine free.

QUERIES. Why can you not collect chlorine over water or mercury? How can you collect hydrogen by displacement?

92. Properties. — Chlorine is a heavy, greenish-yellow gas having a strong and suffocating odor, and producing great irritation to the lining membranes of the throat and nostrils; and, when inhaled in sufficient quantities, it is capable even of producing suffocation and death.

EXP. 71 P. Write with an organic (carmine) ink upon a slip of printed paper; moisten, and hold it in a large test-tube full of chlorine gas. The writing disappears and the printing remains. Printer's ink is made of lampblack (carbon), and is not bleached.

QUERIES. How can you distinguish between organic and mineral colors? Try wall paper. Would chlorine water answer as well?

Chlorine in the presence of moisture is an invaluable bleaching reagent, acting upon vegetable coloring-matters thus: —

$$2\,Cl + H_2O = 2\,HCl + O.$$

Now this oxygen (liberated, as it is, within the fibres of the substance to be bleached), while in a nascent condition, seizes upon the coloring-matters, and destroys them, or changes them into colorless compounds.

EXP. 72 T. Saturate with hot turpentine, $C_{10}H_{16}$, a strip of blotting-paper, and plunge it into a jar of dry chlorine gas.

The turpentine takes fire, the chlorine and hydrogen uniting, while carbon is deposited as soot.

SUG. Student, write the equation.

EXP. 73 P. Plunge a lighted taper into a large test-tube of chlorine. It continues to burn with a dull, red, smoky flame, the chlorine again uniting with the hydrogen contained in the substance of which the taper is composed, while the carbon is set free.

REM. Oils, resins, gums, waxes, tallows, etc., are compounds containing C, H, and O, in varying proportions.

We thus see that chlorine possesses a powerful chemism for hydrogen, even decomposing compounds to obtain it. We shall hereafter see that the great chemism of chlorine enables it to displace from their binary compounds the nearly-allied elements, bromine and iodine. The sulphides are also dissociated thus: —

$$H_2S + 2\,Cl = 2\,HCl + S.$$

Chlorine is extensively used as a deodorizer and disinfectant, owing its efficiency to its power of liberating from water oxygen, which, as already explained, while in a nascent state, oxidizes putrefactive vapors and disease germs to their destruction.

Chlorine is soluble in water, 1^{cc} of water absorbing nearly 3^{cc} of this gas. It may be condensed to a liquid at 0° by a pressure of 6 atmospheres, or by 1 atmosphere at $-34°$. 1^{l} at 0° and 760^{mm} weighs 3.173^{g}, and its specific gravity is 2.450.

93. Tests for Chlorine. — Free chlorine gas or its aqueous solution may be recognized by its color, odor, or behavior, as in the preceding experiments.

CHLORINE AND HYDROGEN.

HYDROCHLORIC ACID, HCl.

94. **Occurrence and Preparation.** — We now come to an important and useful acid, the only compound formed by hydrogen and chlorine, — hydrochloric acid, HCl. This acid rarely occurs in nature, although it is a staple article of commerce. The following is the general method of its preparation: —

EXP. 74 T. Heat to redness, in a crucible, 5^g of common salt, NaCl; pulverize, and place in a generating-flask. Now add 10^g strong sulphuric acid, H_2SO_4, and heat gently. Hydrochloric acid, in the form of a gas, is freely given off, and can be collected by displacement, or over mercury.

By passing through two or three wash bottles, it may be obtained in aqueous solution, the form in which it is used and found for sale. The reaction is: —

$$NaCl + H_2SO_4 = HNaSO_4 + HCl.$$

If a larger proportion of salt be used, the reaction may be represented by this equation: —

$$2\ NaCl + H_2SO_4 = Na_2SO_4 + 2\ HCl.$$

As we shall hereafter see, commercial hydrochloric acid is almost exclusively obtained as a by-product of the alkali works where common "soda" is prepared.

95. **Properties.** — Hydrochloric acid gas is extremely soluble, 1^{cc} water at 0° dissolving no less than 505^{cc} of this gas. Its specific gravity is 1.247, it condenses at $-4°$ under 25 atmospheres pressure, and 1^l weighs 1.632^g.

The aqueous solution of hydrochloric acid is one of the most useful chemicals. It acts upon bases to form chlorides; the principal one of these, common salt or sodium chloride, $NaCl$, occurs in nature in large quantities. The gas has a pungent odor. In contact with the air it forms dense white fumes, in consequence of its attraction for water. The strong water solutions give off the gas readily; weak ones may be concentrated by boiling.

EXP. 75 P. Take three test-tubes. In the first, place a solution of silver nitrate, $AgNO_3$; in the second, a solution of mercurous nitrate, $Hg_2(NO_3)_2$; and in the third, a solution of plumbic acetate, $Pb(C_2H_3O_2)_2$. To all three now add hydrochloric acid. What takes place?

As the silver, lead, and mercurous chlorides are insoluble in water, it precipitates these metals from solutions in which they are contained. Other chlorides, as a rule, are soluble.

This fact is taken advantage of in analyzing unknown substances. Suppose, for example, we have a solution which may contain any or all known metals. If we add hydrochloric acid to it, and get a precipitate, we know that one or more of the metals whose chlorides are insoluble in water must be present. We know, in other words, that one or more of the three metals, silver, lead, and mercury, must be present; and further, as their chlorides are insoluble, we know that the addition of hydrochloric acid to the solution removes these metals. By the use of other chemical substances, other groups may be precipitated in a similar way; and thus the problem of determining what is in the substance under examination is more and more narrowed down, until we know exactly what is present. Substances which are used for the purpose of precipitating groups of metals in analysis are called GROUP-REAGENTS.

When hydrochloric acid is mixed with one-third its volume of nitric acid, AQUA REGIA or *nitro-hydrochloric acid* is produced, which is the strongest solvent known; even gold and platinum are dissolved in it. The great power of aqua regia lies in the fact that it readily gives up chlorine, which, in a nascent condition, is very active. The salts formed by aqua regia are chlorides. In using this solvent it should be but slightly warmed; a stronger heat drives off chlorine to waste.

96. Test for Hydrochloric Acid, or Chlorides. — Their solutions, even when acidulated with nitric acid, give a white precipitate of silver chloride, $AgCl$, with silver nitrate, $AgNO_3$. This precipitate is insoluble in nitric acid, and soluble in ammonia.

SUG. Student, try a solution of $NaCl$. Write the equation.

CHLORINE AND OXYGEN.

97. Chlorine and oxygen unite to form three compounds, which have been isolated, viz., —

	Chlorine monoxide	Cl_2O,
	Chlorine trioxide (?)	Cl_2O_3,
and	Chlorine tetroxide	Cl_2O_4.

These oxides never occur free in nature, nor can they be produced by the direct union of chlorine and oxygen; they may, however, be obtained by indirect processes. Since they are unimportant, and dangerous to prepare, owing to the ease with which they decompose, we shall treat each but briefly.

98. Chlorine Monoxide, Cl_2O. — This substance is a yellow-colored gas, prepared by passing chlorine gas over dry mercuric oxide in the cold, thus: —

$$HgO + 4\,Cl = HgCl_2 + Cl_2O.$$

This gas may be pressed into a U-tube, surrounded with a freezing mixture, and condensed to a yellow liquid; but if the tube be suddenly jarred or scratched, as with a file, it explodes with great violence. If exposed to direct sunlight, it is also decomposed, but without explosion. It unites with water, thus: —

$$Cl_2O + H_2O = 2\,HClO. \quad \text{(See Hypochlorous Acid.)}$$

99. Chlorine Trioxide, Cl_2O_3. — This is a greenish-yellow gas, of great instability and explosive power. It can be prepared in different ways, one of which is as follows: Make a thin paste of 4 parts potassium chlorate, $KClO_3$, and 3 parts of arsenious oxide, As_2O_3, with water; place in a generating-flask, and add a solution of 12 parts nitric acid and 4 parts water; warm gently. This gas may also be condensed to a liquid, but, owing to its extremely uncertain and explosive propensities, the student should not attempt its preparation.

It unites with water, forming chlorous acid, thus: —

$$Cl_2O_3 + H_2O = 2\,HClO_2. \quad \text{(See Chlorous Acid.)}$$

100. Chlorine Tetroxide, Cl_2O_4 **or** ClO_2. — This is a dark-yellow gas of small importance, as it forms no acids, and consequently no distinct series of salts (it is also dangerously explosive); but some idea of its deportment, as well as that of the other chlorine oxides, may be gained by the following experiment, which may be safely made if care be used: —

Exp. 76 p. Drop into a test-tube three or four small crystals of potassium chlorate, $KClO_3$; then, holding the tube with a pair of tongs, its mouth turned away from all persons present, add a few drops of strong sulphuric acid. Warm gently, when chlorine tetroxide gas will appear; but a sharp and vicious explosion soon terminates the experiment. The contents of the tube are thrown violently out, but the tube itself is seldom broken. Note the odor of the gas.

THE CHLORINE OXACIDS.

101. This series contains four acids, none of which are of commercial importance, nor are they of special value as reagents; and they all decompose upon standing. Their salts, however, are stable, well known, and of great utility. These acids are: —

	Hypochlorous acid	$HClO$,
	Chlorous acid	$HClO_2$,
	Chloric acid	$HClO_3$,
and	Perchloric acid	$HClO_4$.

Sug. Student, name the salts these acids form with potassium.

Hypochlorous Acid, $HClO$.

102. Preparation. — This acid has been prepared only in dilute aqueous solution. Owing to its instability, the student must prepare it freshly for the purpose of studying its properties. It is obtained by treating freshly-precipitated mercuric oxide, HgO, with chlorine water, thus: —

$$3\,HgO + 4\,Cl + H_2O = 2\,HgO,\ HgCl + 2\,HClO.$$

Exp. 77 t. Dissolve as much mercuric chloride, $HgCl_2$, as possible in 250^{cc} hot water; then add KOH as long as a precipitate (yellowish-red) is formed. You thus obtain the fresh mercuric oxide: —

$$2\,KOH + HgCl_2 = HgO + 2\,KCl + H_2O.$$

Filter out this precipitate, and wash it by adding much water to it as it lies upon the filter-paper. Finally make a hole in the point of the filter-paper, and wash the precipitate through into a half-litre flask by means of 250^{cc} cold water. Then gradually add chlorine water, thoroughly shaking meanwhile, until the remaining brownish-red precipitate ceases to dissolve (*i.e.*, be careful to keep an excess of HgO. If the chlorine water be fairly-well saturated, you will require less than 200^{cc}). The remaining precipitate is the compound represented by the formula HgO, HgCl. Allow the flask to stand in a cool place until this precipitate settles, when you will be able to pour off the slightly-colored aqueous solution of hypochlorous acid, which may be used for experimental purposes. Note the odor of the acid differing from chlorine.

Exp. 78 p. In a florence flask fitted with a bent delivery tube, generate chlorine gas from sodium chloride, manganese dioxide, and sulphuric acid. Pass this gas into a cold, dilute solution of potassium hydroxide, stopping short of saturation. You will thus obtain for experimental purposes a solution of potassium hypochlorite, KClO, thus: —

$$2\,KOH + 2\,Cl = KClO + KCl + H_2O.$$

103. **Properties.** — Hypochlorous acid, when in dilute aqueous solution, is a yellowish liquid, possessing a characteristic odor and strong bleaching properties. A concentrated solution cannot be distilled without undergoing decomposition; indeed, it soon decomposes at ordinary temperatures, of its own accord, giving off chlorine and oxygen gases.

Exp. 79 p. Moisten in dilute hydrochloric acid pieces of unbleached cotton cloth and suspend them for a moment in the solutions of hypochlorous acid and potassium hypochlorite, as prepared above. Finally wash them in pure water, allow them to dry, and note that they are bleached. Also make this experiment with a solution of bleaching-powder.

The hypochlorites are of great importance, especially the calcium compound, which is used in bleaching-factories under the name of *bleaching-powder*. Enormous quantities of this powder are prepared by passing chlorine gas into chambers containing slaked lime, $Ca(OH)_2$, thus: —

$$2\ Ca(OH)_2 + 4\ Cl = 2\ H_2O + (CaCl_2 + Ca(ClO)_2).$$

It thus appears that bleaching-powder is a mixture of calcium hypochlorite with calcium chloride.

The cloth to be bleached, after a thorough cleansing, is drawn through a solution of bleaching-powder, and then through very dilute sulphuric acid, which decomposes the powder, liberating free chlorine in the fibres of the cloth. By this means, as previously explained, the coloring-matters are destroyed. The effect, upon hypochlorous acid or the hypochlorites, of stronger acids may be seen, thus: —

$$HClO + HCl = H_2O + 2\ Cl,$$

and

$$KClO + 2\ HCl = KCl + H_2O + 2\ Cl.$$

104. Tests for Hypochlorous Acid, or the Hypochlorites. — 1. An aqueous solution of the free acid bleaches litmus paper or solution.

2. The odor of the free acid identifies it.

3. Hypochlorites in solution require acidulating with an acid, as acetic or hydrochloric acid, before they produce their bleaching effects.

QUERY. Will a hypochlorite bleach when acidified with HNO_3? H_2SO_4? Try it.

SUG. Carefully distinguish between *bleaching* a substance and *changing* its color, as from blue to red. When it has been bleached, an alkali will not restore the original color; when simply changed, the color may thus be restored.

CHLOROUS ACID, $HClO_2$.

105. This acid and the salts it forms are unimportant. As already explained, it may be obtained by dissolving chlorine trioxide in cold water, but it does not bear concentration. It is readily decomposed by heat, as likewise are its salts, the chlorites. It also possesses bleaching properties. Its action upon the alkaline bases is very slow and feeble.

106. Tests for Chlorous Acid and the Chlorites. — Test as for a hypochlorite, when the same results are obtained. Then to a fresh portion add a small quantity of arsenious oxide, As_2O_3, and a drop or two of nitric acid. If the solution be that of a hypochlorite, its bleaching power is destroyed. If that of a chlorite, it will still bleach.

NOTE. This acid and its salts may well be dismissed with simply a reading of the two preceding paragraphs.

CHLORIC ACID, $HClO_3$.

107. This acid is also unimportant, and, moreover, somewhat dangerous to experiment upon; its preparation, therefore, should be omitted.

Potassium chlorate, $KClO_3$, the most important salt of chloric acid, is made by passing chlorine into a concentrated, warm solution of potassium hydroxide, KOH: —

$$6\,Cl + 6\,KOH = 5\,KCl + 3\,H_2O + KClO_3.$$

QUERY. What takes place when the solution of potassium hydroxide is cold and dilute?

In order to get the free acid from this potassium salt, the latter is treated with a solution of hydrofluo-silicic acid, H_2SiF_6: —

$$2\,KClO_3 + H_2SiF_6 = K_2SiF_6 + 2\,HClO_3.$$

The potassium salt thus formed is insoluble; consequently, after it has subsided, the dilute solution of chloric acid may be poured off, and afterwards concentrated in a vacuum over sulphuric acid.

Concentrated chloric acid is, indeed, a powerful oxidizing agent, uniting so eagerly with vegetable tissue, as paper and wood, that it ignites them.

Sug. Student, name the uses of $KClO_3$ as suggested by the experiments up to this point.

108. Tests for Chloric Acid and the Chlorates. — 1. Free concentrated chloric acid may be recognized by its odor and by its charring a slip of paper.

2. The dry chlorates, when treated with strong sulphuric acid, yield a yellowish, explosive gas, Cl_2O_4 (see Exp. 76); with hydrochloric acid, they yield free chlorine gas. (Exp. 69.)

PERCHLORIC ACID, $HClO_4$.

109. This acid and its salts are also of but small importance, and the free acid should not be prepared. It is to be had by distilling dry potassium perchlorate, $KClO_4$, with strong, boiled sulphuric acid. Perchloric acid is one of the most powerful oxidizing agents known. When dropped upon charcoal, it explodes with violence, while dry wood and paper are instantly ignited. Upon the skin it produces deep and dangerous wounds.

One of its salts, potassium perchlorate, may be prepared as follows: —

EXP. 80 P. Heat in a generating-flask 5^g potassium chlorate, carefully noting when the oxygen ceases readily to be evolved, and the mass becomes pasty or semi-solid, —

$$2\,KClO_3 = KCl + KClO_4 + 2\,O.$$

Remove the heat, allow the flask to cool, and dissolve its contents in much hot water. Upon cooling, the potassium perchlorate separates out in crystals, while the potassium chloride remains in solution. These crystals may be removed, dried, and used for experimental purposes.

110. Tests for Perchlorates. — 1. Dry perchlorates yield no yellow explosive gas with sulphuric acid, and with hydrochloric acid yield no free chlorine.

2. They require for their decomposition a higher temperature than the chlorates.

CHLORINE AND NITROGEN.

111. Chlorine and nitrogen unite to form a dangerous explosive, which rivals nitro-glycerine, and whose composition is not definitely known. It is prepared by passing a current of chlorine through a moderately warm solution of ammonium chloride. Under no circumstances should the student thus bring these chemicals together. The eminent chemists, Dulong, Davy, and Faraday, were seriously maimed while experimenting with this capricious compound.

EXERCISES IN CHLORINE.

1. *Given:* NaCl, H_2SO_4, MnO_2, HgO, As_2O_3, and KOH. From these chemicals show how you could prepare chlorine and all the compounds treated in this chapter.

2. PROB. How many tons of salt, NaCl, would it require to prepare 10 tons of hydrochloric acid?

3. PROB. How many litres of chlorine gas can be obtained from 75^k of NaCl when the barometer reads 755^{mm} and the thermometer 18° C.?

4. How are acids formed from their anhydrides?

5. *Given:* The formula of an acid to determine the formula of its anhydride. Proceed thus: $2\,HNO_3 - H_2O = N_2O_5$. In a like manner

determine the anhydrides of $HClO_4$, HNO_3, H_2SO_4, HClO, $HClO_3$, and HIO_3.

6. What per cent of HCl is hydrogen? Chlorine?

7. Determine the percentages of H, N, and O in the nitrogen oxacids.

8. PROB. 20^l of Cl, measured at standard temperature and pressure, increased to 20.5^l owing to a fall in the barometer. How many millimetres did the barometer fall?

9. Chlorine gas was discovered in 1774. Who was its discoverer? He used the chemicals HCl and MnO_2. Describe the process, and write the equation.

10. An aqueous solution of chlorine changes, upon standing, to an aqueous solution of HCl. What gas is liberated? Write the equation.

11. How can you prepare chlorine gas from bleaching-powder?

12. The water analyst, in determining by *titration* the amount of chlorine in drinking-water, proceeds thus: He first prepares a standard solution of silver nitrate, by dissolving 4.79^g $AgNO_3$ in 1^l of distilled water; he then measures out 70^{cc} of the drinking-water, and adds sufficient potassium chromate, K_2CrO_4, to tinge the water light-yellow. Now, from a burette graduated to tenths of a cubic centimetre, he adds to the water thus prepared the standard silver solution, drop by drop, with constant stirring, until the red color at first formed in the liquid becomes permanent. The number of cubic centimetres silver solution added is equal to the number of grains of chlorine per imperial gallon. How much silver nitrate does 1^{cc} of the standard solution contain? How much silver? Show how this amount of silver will precipitate 1^{mg} of chlorine. (SUG. 108^{mgs} of Ag precipitate 35.5^{mgs} of Cl; therefore, to precipitate 1^{mg} of Cl requires $108 \div 35.5 = 3.03^{mgs}$ Ag.) The permanent red color is due to the formation of silver chromate, Ag_2CrO_4; this formation does not occur until the chlorine is all precipitated. The potassium chromate thus serves as an *indicator*, showing when the right amount of $AgNO_3$ has been added. Why does the silver unite with the chlorine first?

GENERAL NOTE. Recent investigators doubt the existence in a free state of chlorine trioxide.

CHAPTER VII.

BROMINE, ITS OCCURRENCE, ETC.—THE BROMINE ACIDS.

BROMINE.

SYMBOL Br′.—ATOMIC WEIGHT, 80; SPECIFIC GRAVITY, 3.1872.

112. Occurrence.—Bromine does not occur in a free condition, but is found combined with magnesium, sodium, potassium, and perhaps with some organic compounds, as bromides in sea water, certain mineral waters, and in most saline deposits. It also occurs combined with silver in the silver mines of Mexico and South America.

Balard, in 1826, discovered bromine in sea water. He obtained it from the concentrated solution or "mother liquor" from which the crystals of common salt, $NaCl$, had been removed.

Bromine, although by no means a plentiful element, is, nevertheless, an article of commerce, considerable quantities of it being produced from the concentrated "mother liquors" of salt wells in various parts of the world. The United States produces the greater part of the commercial article.

113. Preparation.—EXP. 81 P. Dissolve in a test-tube a crystal of potassium bromide, KBr; add a small quantity of chlorine water. Notice that the liquid turns somewhat darker than the chlorine water added; this is due to free bromine. Now add three or four drops of carbon bisulphide, CS_2, and shake thoroughly. What color does the carbon bisulphide assume?

EXP. 82 T. Thoroughly mix 30^{g} granulated manganese dioxide, MnO_2, with 40^{g} potassium bromide, KBr, and place in a retort. Use the same apparatus as for nitric acid, excepting that the condenser must contain 0.4^{l} cold water, and the neck of the retort must dip below the water in the condenser; or a rubber cork with a bent tube dipping below the water may be fitted into the neck of the retort. Now pour into the retort 105^{g} sulphuric acid, H_2SO_4, previously diluted with 70^{cc} water, and warm gently. Bromine will distil over in reddish-brown fumes and condense under the water in the condenser. A part of the bromine will also be dissolved in the water, thus giving bromine and bromine water at one operation. Save them both, each in separate bottles accurately fitted with ground glass stoppers, and keep in a cool place.

QUERY. The specific gravity of the H_2SO_4 is 1.84. How many cubic centimetres equals 10.5^{g}?

Bromine is best prepared for class purposes by treating potassium bromide, KBr, with manganese dioxide and sulphuric acid, thus: —

$$3H_2SO_4 + 2KBr + MnO_2 = MnSO_4 + 2HKSO_4 + 2H_2O + 2Br.$$

SUG. Student compare this equation with that given in Preparation of Chlorine, Art. 90.

Bromine is liberated when occurring in saline waters, by adding a small quantity of manganese dioxide, and then just enough sulphuric acid to liberate sufficient chlorine to free the bromine. This process depends upon the fact that free chlorine gas liberates bromine from its compounds.

QUERY. Which possesses the greater chemism, chlorine or bromine?

114. Properties of Bromine. — Bromine is a dark-red colored liquid, at ordinary temperatures always giving off pungent, irritating fumes. It bleaches organic coloring-matter, but not so powerfully as chlorine. Its principal use is as a disinfectant.

Bromine has a specific gravity of 3.1872 at 0°, freezes at – 7.5°, and boils at + 59.3°.

NOTE. When removing the stopper of a bottle containing bromine or its aqueous solution, always turn your face away. Why?

115. Tests for Free Bromine. — 1. Free Bromine, even in dilute solutions, when shaken (in a test-tube) with carbon disulphide, CS_2, colors the latter brownish-red.

2. Colors ether yellowish-red, which color is destroyed by shaking with potassium hydroxide, KOH.

3. Colors starch-paste solution orange-yellow.

SUG. Student make these tests upon a dilute solution of the bromine water prepared as above. Also try the bleaching effect as with chlorine.

BROMINE AND HYDROGEN.

116. Hydrobromic Acid, HBr, is the only acid formed by bromine and hydrogen. It is unimportant to the beginner, and he should not attempt its preparation. It is usually obtained by allowing liquid bromine to act upon amorphous phosphorus and water. This is accomplished by placing 10 parts of liquid bromine in a stoppered funnel provided with a stop-cock to allow the bromine to fall drop by drop into a generating-flask containing one part phosphorus and two parts water: —

$$P + 5\,Br + 4\,H_2O = H_3PO_4 + 5\,HBr.$$

What takes place in this reaction can best be understood by considering it in two phases. When bromine acts upon phosphorus the two unite directly, forming either phosphorus tribromide, PBr_3, or the pentabromide, PBr_5, according to the relative quantity of bromine present. Now each of these compounds is decomposed by water, as represented in the following equations: —

$$PBr_3 + 3\,H_2O = H_3PO_3 + 3\,HBr;$$
$$PBr_5 + 4\,H_2O = H_3PO_4 + 5\,HBr.$$

Thus, in each case, all the bromine appears finally in combination with hydrogen in the form of hydrobromic acid.

We should naturally expect that the simplest method for making hydrobromic acid would be like that used for making hydrochloric acid, but strong sulphuric acid decomposes hydrobromic acid, and hence, although the reaction,

$$2\,KBr + H_2SO_4 = K_2SO_4 + 2\,HBr,$$

actually does take place, a further reaction also takes place, as follows: —

$$2\,HBr + H_2SO_4 = 2\,H_2O + SO_2 + 2\,Br,$$

giving the gas, sulphur dioxide, SO_2, and free bromine in the form of vapor, and from these it is very difficult to separate the hydrobromic acid.

This acid is a colorless, irritating gas whose chief interest to us lies in the fact that it yields the salts called *bromides*, some of which are applied to useful purposes, thus: silver bromide, AgBr, is used in photography; potassium bromide is used in medicine; while others, as magnesium bromide, $MgBr_2$, are much esteemed ingredients of certain mineral springs.

Hydrobromic acid is used in organic laboratories, and it is now an article of commerce.

117. Tests for the Bromides.—1. Place the solution in a test-tube, and liberate the bromine by means of chlorine water; then add a few drops of carbon bisulphide, CS_2, and shake thoroughly. The carbon bisulphide is colored brownish-yellow.

NOTE. An excess of Cl must be avoided, otherwise a chloride of bromine is formed which does not color the bisulphide.

2. With silver nitrate, $AgNO_3$, this solution gives a *yellowish-white* precipitate, AgBr, insoluble in nitric acid, difficultly soluble in ammonia, and easily soluble in potassium cyanide, KCy.

QUERY. How do HCl and the chlorides deport themselves with $AgNO_3$, etc.?

NOTE. When bromides and nitrates occur in the same solution, the tests interfere. The bromine may be readily detected, but not so the nitrates, since the H_2SO_4 and $FeSO_4$ liberate free bromine which obscures the ring.

SUG. Student try a bromide as if testing a nitrate.

118. Bromine, Oxygen, and Hydrogen. — No compounds of bromine and oxygen have been isolated, but two, and possibly three, acids have been prepared, viz:—

HBrO, Hypobromous acid,
$HBrO_3$, Bromic acid,
and $HBrO_4$, Perbromic acid.

In regard to the existence of the last there is much doubt.

These acids never occur in nature, and are of small importance to the beginner, so we shall here notice them but briefly.

119. Hypobromous Acid, HBrO, may be prepared in the same way as hypochlorous acid, HClO, thus:—

$$HgO + 4\,Br + H_2O = HgBr_2 + 2\,HBrO. \quad \text{(See HClO.)}$$

It possesses bleaching powers, is of a straw-yellow color, and easily breaks up into water, bromine, and oxygen.

Query. What salts does this acid form?

120. **Bromic Acid,** $HBrO_3$, is formed by treating silver bromate, $AgBrO_3$, with bromine water, thus: —

$$5\,AgBrO_3 + 6\,Br + 3\,H_2O = 5\,AgBr + 6\,HBrO_3.$$

The salts (bromates) formed by this acid somewhat resemble the chlorates in their properties, but are of little importance commercially.

Exp. 83 p. The easiest way to get a bromate is to dissolve bromine in a strong solution of potassium hydroxide, when a mixture of potassium bromate and bromide is formed: —

$$6\,Br + 6\,KOH = 5\,KBr + KBrO_3 + 3\,H_2O.$$

The bromate will soon separate out in crystals, which the student may try as he did the chlorates.

121. **Tests for the Bromates.** — 1. They are decomposed by hydrochloric acid, giving free bromine (which may be detected as in Art. 115).

Query. What effect does HCl have upon $KClO_3$?

2. The bromates yield no explosive gas with sulphuric acid, but they are decomposed, affording free bromine and oxygen.

Query. How does H_2SO_4 affect the chlorates?

EXERCISES IN BROMINE.

1. What chemicals are needed to prepare bromine and its compounds?
2. What per cent of KBr is potassium? Bromine?
3. How many grams of NaBr would be required to prepare 10g Br?
4. Compare the bromine and chlorine acids from a commercial standpoint.

5. What does the word *Bromine* signify?

6. In analyzing a sample of mineral water, a chemist found 0.1678^g bromine per litre. In combining his bases and acids he united this bromine with magnesium. How many grams per litre of magnesium bromide, $MgBr_2$, did he report? *Ans.* 0.1929^g.

7. How many grams of chlorine gas would be required to free the bromine of one gram KBr? ($KBr + Cl = KCl + Br$.)

8. To precipitate all the bromide in 50^{cc} of a solution, required 0.215^g silver nitrate. How much bromine per litre did the solution contain? Sug. 108 parts Ag precipitate 80 parts Br.

9. Try to prepare HBr by passing H_2S through bromine water. Explain the equation,—

$$H_2S + 2\,Br = 2\,HBr + S.$$

Filter the solution and test for HBr. Can you prepare HCl by passing H_2S through chlorine water? Write the equation.

10. Boil in an evaporating dish a mixture of solid $K_2Cr_2O_7$ and H_2SO_4 until the mixture turns bright red. When cool, place a portion of the substance thus formed in a test-tube fitted with a bent delivery tube, and add a solid chloride, as NaCl. Note the bright brownish-red gas evolved:—

$$4\,NaCl + K_2Cr_2O_7 + 3\,H_2SO_4 = \underline{2\,CrO_2Cl_2} + 2\,Na_2SO_4 + K_2SO_4 + 3\,H_2O.$$

Now lead this gas, which becomes plentiful by applying a gentle heat, into a test-tube containing a dilute solution of ammonia. Note the yellow liquid formed:—

$$2\,NH_3 + 2\,H_2O + CrO_2Cl_2 = \underline{(NH_4)_2CrO_4} + 2\,HCl.$$

Acidify this solution with acetic acid, and add lead acetate:—

$$Pb(C_2H_3O_2)_2 + (NH_4)_2CrO_4 = \underline{PbCrO_4} + 2\,NH_4C_2H_3O_2.$$

Note the yellow precipitate thus obtained.

Thus try with KBr instead of NaCl. What results? Try the same with a mixture of KBr and NaCl. Do you obtain the same reaction as with NaCl alone? How can you distinguish a chloride in presence of a bromide? See Douglas and Prescott, *Qual. Anal.*, p. 159.

CHAPTER VIII.

IODINE. — THE IODINE ACIDS. — SEPARATION OF CHLORIDES, BROMIDES, AND IODIDES. — FLUORINE. — HYDROFLUORIC ACID.

IODINE.

SYMBOL I'. — ATOMIC WEIGHT, 127; SPECIFIC GRAVITY, 4.948.

122. Occurrence. — Iodine, like bromine and chlorine, does not occur free. It is chiefly obtained from sea water, from which it is taken up by seaweeds. These weeds, especially on the coasts of Ireland and Scotland, are washed ashore during storms; then they are collected, placed in shallow trenches, dried and burned in thin layers so that the temperature may not rise high enough to vaporize the iodides of sodium, potassium, etc., contained in the ashes or *kelp*, as it is popularly termed. These iodides are soluble in water, and are removed, by washing, from the ashes. Small quantities of bromides are also obtained in this process. Plantations of this seaweed are cultivated in some parts of the ocean, and at the proper times vessels are sent to collect the weed.

Iodine also occurs together with Chili saltpetre in the form of sodium iodide, NaI, and of late a considerable quantity of that which comes into the market has been obtained from this source. It also occurs as silver iodide, AgI, in certain American silver mines.

123. Preparation. — Exp. 84 p. Treat a crystal of potassium iodide, KI, as in Exp. 81. What results do you obtain?

Exp. 85 t. It is not necessary to prepare iodine for class purposes, since it is an article of commerce, procurable at any drug store. It may be readily obtained, however, by treating potassium iodide, KI, with manganese dioxide and sulphuric acid, as in preparing bromine and chlorine. The iodine vapors may be condensed in a suitable flask surrounded by a cooling mixture.

Commercial iodine is prepared from the iodides by treating them, as above, in iron retorts, when it is liberated in violet vapors and condensed in black, shining crystals upon the sides of suitable condensers: —

$$2\,KI + MnO_2 + 3\,H_2SO_4 = MnSO_4 + 2\,HKSO_4 + 2\,H_2O + 2\,I.$$

Sug. Compare this equation with that for bromine and chlorine.

124. Properties. — Exp. 86 p. Heat a small crystal of iodine in a test-tube. What is the color of the vapor? Note the odor.

Iodine at ordinary temperatures is a black, shining solid, possessing a decidedly metallic appearance, and always giving off fumes of a peculiar odor. When heated, iodine is easily converted into vapor of a splendid violet color and characteristic odor. The specific gravity of this vapor is 8.72.

Query. Courtois discovered iodine in the year 1811. He named it from *ἰώδης, violet-colored.* Why did he thus name it?

Iodine is much used in medicine for various purposes, especially in reducing swellings, such as goitre and weeping sinews. It is also used in checking the spread of eruptive diseases, like erysipelas. When thus applied it is used in the form of a solution prepared by taking, by weight: iodine, 20 parts; potassium iodide, 30 parts; water, 900 parts. Free iodine when brought in contact with the skin turns it brown.

Iodine is only slightly soluble in water, but easily soluble in alcohol, carbon bisulphide, chloroform, and in an aqueous solution of potassium iodide.

125. **Tests for Free Iodine.** — 1. Free iodine colors carbon bisulphide, CS_2, violet.

2. Colors starch paste blue.

NOTE. Those substances heretofore mentioned as coloring a solution of starch paste and potassium iodide blue, produce this effect by liberating iodine which unites with the starch to form a blue substance.

QUERY. What substances act in this way?

IODINE AND HYDROGEN.

126. **Hydriodic Acid,** HI, is the only compound of hydrogen and iodine. This is a colorless gas resembling hydrochloric acid. It is of no commercial importance, owing to its instability. Its principal use is for organic work and as a blow-pipe reagent.

Exp. 87 P. Suspend in a test-tube half full of cold water a few crystals of iodine. Pass through this solution sufficient sulphuretted hydrogen, H_2S (Art. 167), to decolorize it. Hydriodic acid will be formed and sulphur deposited: —

$$H_2S + 2\,I = S + 2\,HI.$$

The sulphur will soon subside, and the clear solution of the acid may be poured off. Reserve this solution for the next experiment.

Hydriodic acid may also be made by the method which was described under hydrobromic acid; that is, by gradually adding iodine to amorphous phosphorus under water. The reactions are the same as in the case of bromine, the iodides of phosphorus being first formed, but afterwards decomposed by the water.

EXP. 88 P. In one test-tube place a solution of mercuric chloride, $HgCl_2$; in another, a solution of silver nitrate, $AgNO_3$; in a third, a solution of lead acetate, $Pb(C_2H_3O_2)_2$. To each of these now add a portion of the hydriodic acid solution prepared as above. Note the brilliantly colored precipitates which are respectively the *iodides* of mercury, silver, and lead. Repeat the experiment, using a solution of potassium iodide, KI, in place of the acid. Do you obtain the same results?

Hydriodic acid unites with bases to form the iodides, many of which are valuable. Some of these iodides possess very bright and distinctive colors which are of service in identifying some of the metals whose salts are in the solution to be analyzed. Since the acid itself is unstable and somewhat troublesome to prepare, the chemist preferably uses a solution of potassium iodide for this purpose.

SUG. Explain these equations:—

$$HgCl_2 + 2\,HI = HgI_2 + 2\,HCl;$$
$$Pb(C_2H_3O_2)_2 + 2\,HI = PbI_2 + 2\,HC_2H_3O_2;$$
$$AgNO_3 + HI = AgI + HNO_3.$$

Also write the same equations with KI in place of HI.

127. Tests for Hydriodic Acid or the Iodides.—1. To the solution add chlorine water. Then add a few drops of carbon bisulphide and shake. Iodine is freed and colors the bisulphide violet.

NOTE. If the iodide is not readily soluble, the iodine may be freed by warming the insoluble iodide in a test-tube with a crystal of potassium chlorate and hydrochloric acid; the bisulphide may then be directly added.

2. With silver nitrate, $AgNO_3$, a yellow precipitate is given, insoluble in nitric acid; sparingly soluble in ammonia; soluble in potassium cyanide, KCy.

Sug. Compare this test with the similar ones for chlorine and bromine.

Query. Which test in the case of chlorine is distinctive? Of bromine? Of iodine?

Note. Solutions of iodides and nitrates do not readily yield a test for nitric acid for the same reasons as those given under bromine. The test for the iodide is readily obtained. Try a solution of KI as for a nitrate. Try a solution of KI and KBr with CS_2, etc. Which test do you obtain?

128. Detection of Chlorides, Bromides, and Iodides in the same Solution. — The student is probably aware that the precipitates obtained with silver nitrate do not afford sufficiently marked characteristics to distinguish these compounds, and that the carbon bisulphide tests also fail, especially in the case of bromides in presence of iodides. To separate and distinguish these substances is not an easy task, and of the many ways proposed, none are entirely satisfactory and at the same time simple and convenient. The following method requires careful manipulation.

Exp. 89 p. Let us suppose the solution to contain NaCl, KBr, and KI. Divide it in three portions and add to numbers 1 and 2 an excess of silver nitrate, when the precipitates obtained in each will consist of AgCl, AgBr, and AgI. Filter out these precipitates and wash them thoroughly with hot water, then wash them through a hole in the point of the filter-paper into separate beakers. To the first beaker now cautiously add but *two* or *three* drops of potassium bromide, and to the second carefully add *three* or *four* drops of potassium iodide, and boil for a short time. Again filter the contents of the first beaker, and test the clear liquid which runs through for chlorides, Art. 96. Filter the contents of the second beaker, and test the solution for bromides (Art. 117, 1).

Try a part of the third portion directly for iodides by Art. 127, 1. In case you do not succeed, proceed thus: To the remainder of the third add a few drops of ferrous sulphate, $FeSO_4$, and copper sulphate, $CuSO_4$, when a light-green precipitate of cuprous iodide, Cu_2I_2, will be thrown down. Test this insoluble iodide by Art. 127, 1, Note.

Explanation. What occurs in the three cases may thus be explained: —

1. In number 1, $AgCl + AgBr + AgI + KBr = AgI + 2\,AgBr + KCl$.

The KBr and AgCl react, yielding KCl, which is soluble and in the solution tested for chlorides.

2. $AgCl + AgBr + AgI + 2\,KI = 3\,AgI + KBr + KCl$.

The KCl and KBr are soluble and readily yield the test for bromides.

3. This last is readily understood when we remember that the iodine is partially precipitated in the Cu_2I_2.

Note. The foregoing method is not sufficiently accurate for quantitative determinations where an *excess* of potassium bromide or iodide would necessarily be employed. Care must be used to avoid an excess of either reagent when employed for qualitative work.

IODINE AND OXYGEN.

129. There is but one known oxide of iodine, Iodine Pentoxide, I_2O_5. This oxide may be obtained by heating iodic acid, HIO_3 as described in the next article.

IODINE, OXYGEN, AND HYDROGEN.

130. There are but two oxygen acids of iodine, viz: —

Iodic Acid, HIO_3,
Periodic Acid, HIO_4.

These acids and their salts are unimportant; we shall therefore notice only the first, and that but briefly.

Exp. 90 op. Heat one part, by weight, of free iodine with ten parts strong nitric acid (sp. grav. 1.5) until red fumes cease to come off and the iodine is dissolved. Evaporate the solution to dryness and heat in the air-bath to 200°. The resulting white powder is iodine pentoxide.

The first product formed in this process is iodic acid, HIO_3. When this acid is heated to 200° it breaks up into water and iodine pentoxide: —

$$2\,HIO_3 = I_2O_5 + H_2O.$$

By again dissolving the pentoxide in water, pure iodic acid may be obtained.

Sug. Write the equation for the action of iodine on nitric acid, remembering that NO, HIO_3, and H_2O are formed. Also show the action of H_2O on I_2O_5.

Iodic acid rapidly oxidizes organic substances. When this acid or the pentoxide is heated with powdered charcoal, phosphorus, sulphur, etc., it oxidizes them so rapidly that the action is accompanied by flame.

It forms normal salts, the iodates, as KIO_3. Acid salts, as KIO_3HIO_3 or $HK(IO_3)_2$, are also known.

131. Tests for Iodic Acid or the Iodates. — To a solution containing either the free acid or its salts add starch paste and chlorine water; no change in color occurs. Now add a solution of sodium sulphite, Na_2SO_3, when iodine is liberated and the solution turns blue.

FLUORINE.

SYMBOL, F'.—ATOMIC WEIGHT, 19; SPECIFIC GRAVITY, UNKNOWN.

132. Occurrence.—Free fluorine is unknown. It occurs combined with calcium as calcium fluoride, CaF_2, or fluor spar, in cubical crystals which are usually somewhat translucent and often quite transparent. It also occurs in the mineral cryolite, which is a fluoride of sodium and aluminium. Other sources of fluorine are unimportant.

Fluorine has resisted all attempts to isolate it, and they have been many. This fact appears to be due to its great chemism when nascent, at which time, it invariably attacks and combines with the vessel in which it is generated. Nothing is known of its physical properties, and but little of its chemical deportment other than its great chemism.

Fluorine forms no oxides, no oxygen acids, and but one hydrogen acid, viz.:—

HYDROFLUORIC ACID, HF.

133. Preparation.—This acid is also a gas corresponding to hydrochloric, hydrobromic, or hydriodic acid. It is best prepared by treating calcium fluoride in a leaden evaporating-dish, with sulphuric acid:—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2\,HF.$$

This gas is a dangerous poison, and great care must be exercised in its preparation.

134. Properties.—EXP. 91 T. Pulverize 4^g calcium fluoride, and place in a leaden dish, which can be made by cutting off a piece of lead pipe, splitting it open lengthwise, and then placing it in an iron mortar where it can, by the aid of an iron pestle, be hammered out into the shape of an evaporating-dish. Next prepare a sheet of glass by coating both sides with beeswax or paraffin. Upon one side of this glass engrave, by means of a pin or sharp, soft wire, some design. Now put the evaporating-dish, supported by a ring-stand, in a gas-chamber or where there is a current of air to carry off all fumes, and support the plate a short distance above the dish. Add strong sulphuric acid to the calcium fluoride, when hydrofluoric acid will be quickly liberated, especially if a gentle heat be cautiously applied. In a few minutes the design will be neatly etched into the glass. *Be very careful not to inhale any hydrofluoric acid fumes, as they are exceedingly poisonous.*

Hydrofluoric acid is often employed as above in etching thermometer scales.

This acid seems to have great chemism for such substances as calcium, silicon, and potassium, in consequence of which glass is immediately attacked and can not be used to store the gas or its aqueous solution. Leaden or vulcanite bottles are employed for this purpose.

The action of hydrofluoric acid upon sand and glass, which is a compound of sand with bases, is largely due to the action represented by the equation, —

$$SiO_2 + 4\,HF = 2\,H_2O + SiF_4.$$

The silicon tetrafluoride, SiF_4, thus formed, escapes as a gas.

135. Tests for Hydrofluoric Acid in Fluorides. — The best is the etching test, but care must be taken not to scratch the glass with the graver used in cutting through the wax.

EXERCISES IN IODINE AND FLUORINE.

1. How many grams of silver nitrate would be required exactly to combine with 10^g of potassium iodide?

2. How many pounds of iodine can be obtained from one-half ton of sodium iodide?

3. What chemicals are necessary to prepare from potassium iodide iodine and its compounds?

4. Make a comparison between the commercial values of the acids of chlorine, bromine, and iodine.

5. Compare the same three elements according to their physical conditions at ordinary temperatures; also according to their atomic weights, specific gravities, and chemism. Make a table comprising the acids they form.

6. Will nitro-hydrochloric acid liberate bromine and iodine from their compounds? Try it.

7. Class prepare a sheet of glass as directed in Exp. 91, writing the names of the class through the wax. Under the teacher's direction etch with HF. This will be a good memento to leave in the Laboratory.

8. Test a solution of NaCl and KNO_3 for the different acids combined with bases in these salts.

9. Under potassium and sodium learn the tests for these metals, and try for them in the above solution.

10. It would now be well for the student to practise daily upon *unknown* solutions, as in 8 and 9. These solutions should not contain acids that interfere, and the bases with which the acids are combined should preferably be potassium, sodium, and ammonium.

11. In working upon an unknown solution a student obtained tests for K, Na, NH_3 and H_2SO_4, HCl, and HNO_3. What salts may have been dissolved in the solution? In case the laboratory contains only NH_4NO_3, NH_4Cl, KNO_3, KCl, NaCl, and K_2SO_4, what salts may the teacher have employed in preparing this solution?

12. See *Trans. Roy. Soc. Canada*, 1883, sec. 3, pp. 65 *et seq.*, for "Hydriodic Acid as a Blow-pipe Reagent." Dr. Haanel's paper on this topic is accompanied by very fine plates.

13. To a solution containing an iodide and a bromide add CS_2; now by the addition of sufficient chlorine water try to obtain first the color for iodine, and second the color for bromine. Explain.

CHAPTER IX.

CARBON. — CARBON AND HYDROGEN. — OXIDES OF CARBON. — CARBONIC ACID. — CYANOGEN. — PRUSSIC ACID.

CARBON.

SYMBOL C^{iv}. — ATOMIC WEIGHT, 12. — SPECIFIC GRAVITY: DIAMOND, 3.5–.6; GRAPHITE, 2.25; CHARCOAL, 1.57.

136. Occurrence. — Carbon is a very widely distributed element, occuring chiefly in an impure state or in chemical compounds. It is an important constituent of all organic substances, mineral carbonates, carbonic acid gas, and the cyanides. In a free condition, it exists in three widely differing forms.

1. In pure, transparent, glittering, octahedral crystals, as **Diamonds**, which are found in earthy detritus or clayey shales in Africa, South America, Australia, and other localities.

SUG. Write an essay on diamond-mining, diamond-cutting, and famous diamonds.

2. In dark, shining, six-sided slabs as **Graphite**, Plumbago, or Black Lead, which occurs in England, Ceylon, the United States, and other countries.

3. In impure forms as **Coal**, Soot, and Lamp-black. Of coal we find a number of varieties, as Charcoal, Anthracite coal, Bituminous coal, etc.

SUG. Write a short paper on coal-mining.

137. Preparation. — It is not necessary to prepare carbon for class illustration, since any of the above-named modifications are easily to be obtained.

Small *diamonds* are said to have been made artificially by a somewhat complicated process, which cannot be profitably described at this stage. The method of their formation in nature is not understood.

Graphite has been frequently observed in iron-smelting furnaces, having been artificially produced at high temperatures.

In Exp. 2, *Charcoal* was obtained by heating wood in a test-tube. The principles therein involved are made use of in preparing charcoal for commerce. In practice the wood is heated in closed iron cylinders, or burned in large pits or kilns with a limited supply of air. In the latter case a part of the wood thus treated is completely consumed in order to furnish the heat requisite for charring the remainder.

Lamp-black or *soot* is prepared by burning a carbonaceous substance, such as oil, resin, etc., in a limited supply of air. The lamp-black appears as a black smoke which is easily collected upon a cold surface.

QUERIES. What makes a lamp smoke? Why is the lamp-chimney blackened? Explain the deposition of soot in stovepipes and chimneys. Can soot be obtained from the Bunsen flame? Luminous flame? Alcohol flame? Ordinary candle flame? Why does pitch-pine give such a smoky flame? If one wishes to know a fact which comes within the province of *Experiment*, how should he proceed?

138. Properties. — Carbon is absolutely indispensable to all organic structures. With other elements, such as hydrogen, oxygen, and nitrogen, it is capable of forming an almost endless number of chemical compounds. As a matter of convenience these are generally considered under the head of the *Chemistry of the Compounds of Carbon*, or ORGANIC CHEMISTRY.

Carbon has many industrial uses. It is chiefly used in reducing metals from their ores and for heating and illuminating purposes.

The colorless *diamond* is highly prized as a jewel. A colored variety is used in glass-cutting, while its dust is employed for polishing hard and refractory substances. Drills armed with diamond points are used by miners and others; these drills will quickly cut through the hardest rocks. Smoky or black diamonds and *carbonado*, an impure massive form, are principally used for this latter purpose.

The diamond is the hardest substance known, its value in the "scale of hardness," by which mineralogists estimate the hardness of minerals, being 10°. This scale, in which each substance is able to scratch all that are below it in the scale, is as follows: —

Diamond	10°	Apatite	5°
Sapphire	9°	Fluorspar	4°
Topaz	8°	Calcspar	3°
Quartz	7°	Gypsum	2°
Feldspar	6°	Talc	1°

The primary form of a diamond crystal is octahedral; but it occurs in many different forms derived from this primary crystal. When first removed from its matrix, the diamond is often rough and lustreless, and afterwards requires cutting and polishing; this latter is accomplished by means of its own dust. Like all hard substances it is brittle and quite easily broken. In acids and alkalies the diamond is completely insoluble. When heated to a high temperature in a current of oxygen it burns, the product being carbon-dioxide gas, CO_2, with a small amount of residual ash. Upon light the diamond exerts a very high refractive influence, to which property it owes its great brilliancy.

QUERY. What properties cause the diamond to be so highly esteemed as a jewel?

Graphite is greasy to the touch. It is largely used for polishing purposes, such as for coating shot and powder, and, owing to its great permanence in the air, is largely employed in the manufacture of stove-polish. Its particles, however, are very hard, and the saws used in cutting it are quickly worn out, and a knife, when employed for the same purpose, soon loses its edge.

Graphite, owing to its great infusibility, is now mixed with clay and extensively used in making crucibles which are employed by metallurgists, while its employment in the manufacture of leads for the common lead-pencil is a well-known application.

SUG. Prepare a paper on the manufacture of lead-pencils.

Coal is probably the remains of a magnificent vegetation which flourished during the carboniferous age. It has been brought into its present condition by heat and pressure. The heat is thought to have been supplied by the heated interior of the earth, while the pressure was due to the influence of water and the rocks which subsequently formed above the coal. This explanation contemplates the idea that during some post-carboniferous convulsion which swept over the globe, the land sank down, and the vegetation was overwhelmed by the inrush of water, while the rocks were afterward deposited. The ashes and "clinkers" of burned coal are the mineral sediments which were entangled by the vegetation, as well as the mineral constituents of the plants themselves.

Anthracite coal is used for heating purposes, and for reducing metals from their ores. Its reducing power depends upon the chemism of carbon for oxygen.

QUERY. What is meant by *reduction*?

Bituminous coal differs from anthracite in that the former contains more hydrogen-carbon compounds, and evidently has not been subjected to so high a temperature or to so great a pressure by natural agencies. This variety of coal burns with a very hot and sooty flame, and needs a large supply of air for its combustion.

Coke is a form of carbon obtained by driving off, at a high temperature, the volatile constituents of coking-coal. It is left behind in the retorts when coal is distilled for the purpose of making illuminating-gas.

Gas Carbon is also produced in distilling coal. This form of carbon is much used in making negative plates for batteries and for the terminals of electric lamps.

Peat is a form of fuel nearly akin to bituminous coal, and is formed from the roots and stems of certain plants growing in bogs or marshes.

Lignite is a peculiar form of coal formed from such sources as our present deciduous trees, and often exhibits a distinctly woody structure.

Jet is a black variety of lignite, much used in jewelry. Jet readily takes a high polish.

Lampblack is much used as a paint, and in making printers' ink.

Charcoal is employed as a reducing agent in preparing iron from its ores.

QUERIES. For what purposes do you use charcoal in the laboratory? What class of artisans employ charcoal? What other common uses does it have?

Charcoal possesses some remarkable properties: —

Exp. 92 p. Place a filter-paper in a funnel; then fill the paper nearly full of bone-black or freshly-burned charcoal powder. With a filter thus arranged see if you can produce any changes in the following solutions by filtering them several times: 1. Vinegar; 2. Syrup of brown sugar; 3. Dilute black molasses; 4. Indigo solution; 5. Carmine solution; 6. Beer; 7. Potassium dichromate solution.

Queries. What changes occurred? Does 7 behave like the others? Why? Explain the changes.

We thus see that charcoal is capable of decolorizing and purifying such organic liquids as were mentioned. The reason why it is employed in filtering drinking-water is now apparent. It is supposed that this action of charcoal is partially due to the fact that it absorbs oxygen, and possesses the power of causing certain organic substances to combine with this oxygen. However this may be, the charcoal soon loses its efficacy unless it be frequently washed and exposed to the air. For the same reason charcoal will destroy the gases from putrefying substances.

Queries. Why should a filter be frequently cleaned? Is it best continuously to keep a filter full of water? What is the use of gravel in filters? Why should a rapid river flowing over stones and with numerous falls be purer than one with a sluggish current and a sandy or muddy bottom?

Exp. 93 p. Place in an evaporating-dish a few grains of common sugar; add a few drops of strong sulphuric acid. Do you obtain carbon? Also thus try starch. What results?

From the above experiment and from previous work the student may learn that many substances, such as sugar, oils, resins, fats, waxes, tallow, and alcohol are compounds of carbon. We may add to this list nearly every substance used as food by man and by animals, and all the vegetable drugs known to chemistry and commerce. We should not forget also that it is to the compounds of carbon that we are indebted for our raiment, and even for a portion of our dwellings.

QUERY. How could we obtain light without the aid of carbon?

Kerosene, gasoline, naphtha, benzine, and paraffin are all derived from PETROLEUM, or rock oil, which is a mixture of many compounds of carbon and hydrogen found in company with coal deposits. The limits of our work forbid a further notice of these interesting substances.

139. Tests for Carbon. — 1. Free carbon, as soot, coal, lampblack, etc., may be recognized by its physical properties and by its insolubility in all acids and alkalies; also by the manner in which it burns when heated on platinum foil.

2. Graphite may be recognized by its properties, and by the black, insoluble streak which it leaves when drawn across paper.

SUG. Write with a lead-pencil on white paper. Try to *bleach* it. What results?

3. The diamond is recognized by its brilliancy and hardness, being able to produce a scratch upon the hardest substance.

QUERY. The hardness of glass is less than 6°. Is the fact that a given substance makes a scratch upon glass sufficient evidence that it is a diamond?

CARBON AND HYDROGEN.

140. Carbon and Hydrogen form many compounds, but three of which we shall notice here: —

1. Methane, or Marsh Gas, CH_4;
2. Ethylene, or Olefiant Gas, C_2H_4;
3. Acetylene, C_2H_2.

METHANE, CH_4.

141. Methane, or Marsh Gas, may thus be prepared for illustration: —

EXP. 94 P. 2^g sodium acetate, $NaC_2H_3O_2$, are heated in a hard glass test-tube fitted with a jet, with 8^g sodium hydroxide, NaOH, and 2^g finely-powdered quick-lime, CaO. As soon as the gas issues freely from the jet it may be ignited, when it burns with a bluish-yellow, non-luminous flame. The reaction is —

$$NaC_2H_3O_2 + NaOH = Na_2CO_3 + CH_4.$$

QUERY. What purpose does the CaO serve? (Compare the use of MnO_2 in producing oxygen from $KClO_3$.)

This gas occurs free in nature, and is formed in stagnant pools by the decay of leaves and other vegetable material, whence it derives its name, Marsh Gas. It also occurs in coal seams and in coal mines, where it is known as ***Fire Damp***. Methane condenses at −10° under 50 atmospheres, and boils at −160° under 1 atmosphere.

EXP. 95 P. Discharge the hydrogen pistol by means of a mixture of marsh gas and air.

When mixed with air or oxygen, methane is often the cause of most violent explosions. To prevent these explosions, Sir Humphrey Davy invented his Safety Lamp, which consists of an ordinary lamp, the flame of which is surrounded with a wire-gauze cage. This cage prevents the temperature of the surrounding mixture of methane and air from rising to the point of ignition. The specific gravity of methane is 0.558.

QUERY. Why does the wire gauze placed between the Bunsen flame and chemical vessels prevent them from breaking?

SUG. Student ascertain the particulars of several noted colliery explosions.

EXP. 96 P. Hold moistened strips of red and blue litmus paper in a jet of methane. The gas does not affect them.

We are thus led to the conclusion that methane does not resemble either the acid or the alkaline gases already studied. These compounds of carbon and hydrogen differ in many respects from the compounds of other elements with hydrogen. A very large number of the hydrogen-carbon compounds is known and new ones are being constantly discovered. We may regard as derived from these the compounds treated in organic chemistry.

Since methane is not readily acted upon by reagents, the color of its flame, and its explosiveness when mixed with air, will answer our purposes as *tests*.

ETHYLENE, OR OLEFIANT GAS, C_2H_4.

142. Ethylene is formed in distilling coal, and is, therefore, a constituent of coal gas. It is prepared most readily by the following method, which may be shown for class illustration: —

EXP. 97 T. Heat in a generating-flask fitted with a jet delivery-tube 10^g of ethyl alcohol, C_2H_6O, with 50^g strong sulphuric acid. Note the odor and taste of the gas issuing from the jet, and then ignite it. It burns with the ordinary gas-flame. The sulphuric acid simply abstracts one molecule of water from the alcohol, thus: —

$$C_2H_6O = H_2O + C_2H_4.$$

QUERY. How many cubic centimeters of alcohol and acid are required above, the specific gravity of H_2SO_4 being 1.843 and that of ordinary alcohol being 0.815?

Ethylene is explosive when mixed with three times its volume of oxygen.

QUERY. What substances are formed? Student write the equation.

When equal volumes of ethylene and chlorine gases are brought together, an oily liquid, called "Dutch Liquid," $C_2H_4Cl_2$, the odor of which resembles chloroform, is formed.

The specific gravity of ethylene is 0.9784; it can be condensed to a liquid at 10° by a pressure of 51 atmospheres, and boiling under 1 atmosphere at $-100°$.

143. **Test for Ethylene.** — Fill a jar with the gas supposed to contain ethylene; then pass a current of chlorine gas into the jar. If the oily Dutch Liquid mentioned above be formed, ethylene is present.

NOTE. This liquid is insoluble in water.

ACETYLENE, C_2H_2.

144. **Acetylene** is also a gas, and possesses a powerful and disagreeable odor, which is particularly noticeable when an ordinary Bunsen burner strikes back and continues to burn at the base.

It has been prepared by passing sparks from a powerful battery through an atmosphere of hydrogen, the terminals of the electrodes being carbon. No other hydrocarbon compound has been thus directly produced. It burns with a bright, luminous flame, and has a specific gravity of 0.92. The odor of acetylene betrays its presence.

145. Illuminating Gas is obtained, together with many bye-products, by distilling coal in retorts. It contains hydrogen, methane, and ethylene, and many other hydrocarbon compounds. It also contains in small quantities the impurities: ammonia; hydrogen-sulphide, H_2S; carbon dioxide, CO_2; carbon monoxide, CO; atmospheric oxygen; and nitrogen. These impurities are mostly removed by passing the gas through a series of washing and absorbing reagents.

SUG. Student visit the gas works. Write a description of the process of gas manufacture. Consult R. and S.

The student may test for these impurities thus: —

1. *Ammonia* is detected by holding a strip of moistened faintly-red litmus paper in a stream of the illuminating gas. The paper turns blue if ammonia be present.

2. *Hydrogen sulphide* will blacken a strip of bibulous paper moistened with lead acetate, $Pb(C_2H_3O_2)_2$, when the paper is held in a current of the gas.

3. *Carbon dioxide* may be detected by shaking lime-water, $Ca(OH)_2$, in a flask of the gas (see test for CO_2).

4. *Oxygen* may be detected as directed under tests for oxygen. Art. 29, 2.

5. The nitrogen and carbon monoxide cannot be detected with certainty by any means likely to be at the beginner's disposal.

Coal Tar. — It has been mentioned that there are many bye-products formed in distilling coal in the manufacture of illuminating gas; of these coal tar is, from a chemical standpoint, the most remarkable. It is used directly for various industrial purposes which are so well known as to need no description. The attention of many chemists has been given to this substance, and from it they have produced a large number of articles which are in daily use in the arts and manufactures. The beautiful aniline anthracine and naphthaline dyes are obtained from this source, and their production has revolutionized not only the art of dyeing, but also the industries of whole countries, and made it possible for even the laborer to embellish his home with colors which before were only accessible to the opulent. From coal tar, then, we may see the artificial production of substances which formerly were only obtained from natural sources; and thus is the distinction between the so-called organic and inorganic substances rapidly passing away.

SUG. The student who reads German may obtain valuable information upon this topic by consulting Schultz's *Chemie des Steinkohlentheers.*

QUERY. What are the *natural* sources of indigo? Cochineal?

CARBON AND OXYGEN.

146. There are two oxides of carbon, viz: —

1. Carbon Monoxide, CO;
2. Carbon Dioxide, CO_2.

Of these two oxides the latter is to us of the greater importance. Both are gases under ordinary conditions.

CARBON MONOXIDE, CO.

147. Preparation, etc. — This gas is a product of combustion, and is formed when carbon is burned in a limited supply of oxygen: —

$$C + O = CO.$$

It is also formed at high temperatures by the action of carbon on carbon dioxide: —

$$CO_2 + C = 2\,CO.$$

QUERY. Of what kind of action is this an example?

EXP. 98 P. Carefully heat in a generating-flask with a delivery-tube, 2^g potassium ferrocyanide, K_4FeCy_6, with 20^g strong sulphuric acid. Ignite the stream of escaping gas, CO; carefully note its odor, if any, and the color of the flame.

Carbon monoxide burns with a lambent blue flame, as seen in coal stoves when the supply of air is limited, and at the upper surface of the coal in grate fires. The combustion at the bottom of the coal first produces carbon dioxide; this substance coming in contact with the heated coal near the upper surface is reduced to carbon monoxide; and when this latter meets the air above the coal, it again burns, forming carbon dioxide, the combustion now being complete: —

$$CO + O = CO_2.$$

Carbon monoxide is colorless and tasteless, and has a faint and peculiar odor. It acts upon the animal economy as a deadly poison, producing headache, giddiness, and insensibility. It seems to produce its effects upon the system by combining with the haemoglobin of the blood, leaving traces which betray its action even after death. Great care should be taken not to allow this poisonous gas to accumulate in rooms warmed by coal fires. One per cent is a sufficient quantity to prove fatal. The joints of the stove should be tight, the draft strong, and, above all, the ventilation should be perfect. Death has been produced from warming poorly-ventilated rooms by means of charcoal fires in open vessels from which carbon monoxide is given off; and people have perished by going to sleep beside a lime or brick kiln or a charcoal pit, being suffocated and poisoned by the gaseous oxides of carbon.

Tobacco smoke contains more or less carbon monoxide. Hence, the inhalation of the air of a room in which many persons are smoking may produce pernicious effects upon the system.

Carbon monoxide has a specific gravity of 0.968, and condenses at −139.5°, under a pressure of 35.5 atmospheres; under 1 atmosphere it boils at −190°.

148. Test for Carbon Monoxide. — This gas may be recognized, when present in sufficient quantity, by its bluish flame.

CARBON DIOXIDE, CO_2.

149. Occurrence. — This gas, commonly known as carbonic acid gas, occurs widely distributed in nature. It occurs free in the atmosphere in small but persistent quantities, and combined in all the carbonates, from which it is readily liberated by the stronger acids. Calcium carbonate, or limestone, $CaCO_3$, is a very plentiful substance. Whole geological formations consist of this material. It also is the chief constituent of shells and most corals. Whole islands are being constantly built up by the corals in the tropical regions.

SUG. Write a paper on coral formations.

150. Preparation. — EXP. 99 P. In a wide test-tube or a small beaker place about 5^{cc} calcium hydroxide solution, $Ca(OH)_2$. By means of a small glass tube force air from the lungs through the solution, when a white precipitate will be formed. Continue to breathe some minutes through the liquid; the precipitate dissolves.

This white precipitate is calcium carbonate, $CaCO_3$, and was produced by the action of the carbon dioxide which is thrown out of the lungs as a waste product at every respiration: —

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$

Large quantities of carbon dioxide must thus necessarily be liberated in the air, since it is produced in the same way by all air-breathing animals.

QUERY. Why does the air in poorly-ventilated living-rooms contain more carbon dioxide than those that have good ventilation?

EXP. 100 P. Carefully lower into a wide-mouth bottle a burning taper. When the taper is extinguished, add a small quantity of calcium hydroxide; cork the bottle, and shake. Do you again obtain the white precipitate?

All carbon compounds when burning in the air produce carbon dioxide. This gas is also emitted during volcanic action.

QUERY. In what ways may CO_2 be liberated in living-rooms?

EXP. 101 P. To a dilute solution of sugar or molasses in water add a little bakers' yeast. Place in an evaporating-dish a small quantity of this solution; also fill a test-tube with the solution, invert the tube, and place its mouth below the solution in the evaporating-dish. The whole is now to be left standing in a warm place. *Fermentation* soon begins, bubbles of gas rise in the tube, and the liquid is forced down. When the tube is full of gas, pour the latter out into another tube (as if it were water), add calcium hydroxide, and shake as before. Is the gas carbon dioxide?

Carbon dioxide is also produced in fermentation, and in the spontaneous decomposition of animal and vegetable substances.

QUERY. In what ways is carbon dioxide liberated in the atmosphere?

Exp. 102 p. Break into pieces about 10^g calcium carbonate, or marble, $CaCO_3$. Place in a generating-flask, and cover with water. Fit the flask with a V-shaped delivery-tube, and collect the materials mentioned in the following experiments. Upon adding hydrochloric acid to the contents of the flask, carbon dioxide will be plentifully given off, although a gentle heat may sometimes be required. The equation is: —

$$CaCO_3 + 2\,HCl = CaCl_2 + H_2O + CO_2.$$

Note. The $CaCl_2$ solution should be evaporated to dryness, fused in a sand crucible, and kept in a tightly-corked bottle. It is useful for drying gases and for other purposes.

Carbon dioxide may be readily obtained in larger quantities by treating the carbonates with strong acids. With the gas which the student is now ready to prepare he may proceed to study the

151. Properties. — Exp. 103 p. Fill a wide test-tube with carbon dioxide. Note the odor and color, if any, and try the effect upon a glowing match; a burning match; a lighted taper. What results? Try to ignite a jet of this gas.

Carbon dioxide is a colorless, odorless gas which does not support combustion. Advantage has been taken of this fact in making an engine to extinguish fires. The gas is generated from sodium carbonate, Na_2CO_3, and sulphuric acid, and allowed to escape through a hose.

Sug. Explain the construction of a Babcock fire extinguisher. Write the equation for the reaction of Na_2CO_3 and H_2SO_4. For $HNaCO_3$ and H_2SO_4.

Exp. 104 p. In the centre of a pine ruler 2^{cm} wide and 100^{cm} long drive two needles. This ruler will serve as the beam of a balance, while the needle-points will serve instead of a knife-edge bearing. These points are to be placed upon a flat metallic surface. Now from one end of the beam suspend, by means of a thread, a small paper sack, and from the other end a larger paper sack. Into the smaller sack carefully drop small pieces of iron, chalk, sand, or any heavy substance, until the beam is in equilibrium. Into the larger sack now deliver a jet of carbon dioxide. The larger sack will soon become heavier and sink.

QUERIES. With what gas was the larger sack filled before introducing the CO_2? Is CO_2 lighter or heavier than air? Suppose the sack be suspended mouth downwards, what would occur if a jet of hydrogen were allowed to flow up into it? In what other way have you compared the weight of air with that of gases? How should a jar be placed when filling it with CO_2, mouth down or up?

EXP. 105 P. Place a lighted taper in an open jar of air. Now fill a second jar with carbon dioxide, and then pour the contents of this jar into the first. As soon as the taper is immersed in carbon dioxide it is extinguished. Try to transfer by means of a siphon the contents of a jar of carbon dioxide into another arranged with a taper like the first, treating the gas as if it were a liquid.

Carbon dioxide is heavier than air, its specific gravity being 1.529. 1^l at 0° and 760^{mm} weighs 1.965^g. It can be condensed to a liquid by pressure or by reduction of its temperature. Under one atmosphere it liquefies at $-78°$; a still further reduction, which may be accomplished by allowing the liquid to escape into a box with a sieve-like bottom, freezes the liquid to a snow-like solid.

EXP. 106 OP. Place any small animal in a jar of carbonic acid gas; note the symptoms and time of death. Also thus proceed with a jar of carbon monoxide. How do the symptoms compare? The time of death?

Pure carbon dioxide seems to produce its deadly effects by asphyxiation, the lungs being unable to effect the decomposition of the gas, and thus to appropriate the needed oxygen, which it certainly contains, but holds with an exceedingly tenacious grasp. As one would infer, this gas is very stable; but its decomposition can, nevertheless, be accomplished.

Exp. 107 p. Into a jar of carbon dioxide place a brightly burning magnesium ribbon. It continues to burn. Is carbon set free? Also try a piece of burning sodium. Is the gas again decomposed? Are other products than carbon formed? If these products are MgO and Na_2O, write the equations.

Since carbon dioxide is liberated in so many different ways, it is present in the atmosphere in considerable quantities. It varies from 2.7 to 3.5 volumes in 10,000 volumes of air. This gas is more plentiful in living-rooms than out of doors, but the amount present should never be allowed to exceed 7 or 8 parts per 10,000. It is not so much that carbon dioxide is itself very poisonous, as that other and more dangerous animal impurities are thrown off by the lungs together with the carbon dioxide. We may therefore practically employ the amount of carbon dioxide present in a living-room as an index to measure the purity of the air, as will hereafter be explained.

Prob. Calculate the number of cubic metres of CO_2 in the atmosphere, assuming the extent of the air to be as stated under Atmosphere. Compute its weight.

Carbon dioxide gas is often found in mines, caves, old wells, and vats. When so occurring it is termed *Choke Damp*, and many persons yearly lose their lives through a lack of caution in entering such places. Before venturing into a place where choke damp is likely to occur, it is best to lower a lighted candle; should the candle be extinguished, it is unsafe to go in. A well may sometimes be freed from choke damp by dashing in much water, the gas being thus absorbed; and, again, a vat may be made safe by making an opening in the bottom. Why?

Carbon dioxide is indispensable to plant life. It can be shown that in *sunlight* the leaves, roots, and green parts of plants absorb carbon dioxide and give off oxygen; also on moonlight nights and under the influence of the electric light the same processes go on more slowly; but, in the dark, carbon dioxide is given off, and oxygen is quite freely absorbed.

Sug. Devise an experiment to show the effect of a growing plant, in sunlight, upon carbon dioxide.

Queries. Are plants in a living-room conducive to health? In a sleeping-room? How are plants and animals interdependent through carbon dioxide and oxygen? What prevents the excessive accumulation of carbon dioxide in the atmosphere? What would result if all the oxygen of the air were consumed? All the carbon dioxide? If there were an excess of the latter gas?

Exp. 108 p. Fill a bottle of about 1^l capacity with water, and invert it over the pneumatic trough, or better, over a basin of pure water. Now fill the bottle three-fourths full of carbon dioxide. Cork the bottle with its mouth under water; remove, and shake it thoroughly. Again place the mouth of the bottle under water, and uncork. Does the water rise in the bottle? Is carbon dioxide soluble in water? Reduce the temperature of the bottle by means of a freezing mixture, and shake as before. Again remove the cork under water. Does a greater diminution of the volume of the gas take place? Boil a portion of the water in the bottle, and test by adding calcium hydroxide (Art. 151). Does the boiled water give a reaction? Test a portion of the water in the bottle, with blue litmus paper. Is it acid? Taste of the water in the bottle, or drink of it if you wish. How does it taste?

Note. The gas for this experiment should be washed through a solution of sodium carbonate. Why?

Although carbon dioxide is injurious when inhaled, it is, nevertheless, when taken into the stomach, sometimes an aid to digestion. Certain springs and artesian wells owe their excellent properties to the carbon dioxide absorbed in their waters, while soda water is simply pure water highly charged (under pressure) by this gas.

SUG. Examine and describe a soda-water fountain.

QUERIES. What causes the effervescence of champagne? Beer? Cider? What effect does vinegar produce upon common baking-soda? Can you thus generate carbon dioxide? What causes dough or "emptyings" to rise? By what process is the gas furnished in this latter case? What is meant by *heavy* bread?

Carbon dioxide is soluble in cold water, 1^{cc} of water at 0° dissolving about 1.8^{cc} of the gas; if the pressure be increased, the solubility is also increased. An increase of the temperature of the water drives off the gas, the process being complete at 100°.

QUERIES. What Exp. shows that limestone is soluble in water containing free carbon dioxide, but insoluble in water containing none of this gas? How is the deposition of limestone formations to be explained? How the crust formed in the tea-kettle? The formation of caves?

When carbon dioxide is passed into water, the solution is slightly acid, and it is believed that an acid of the formula H_2CO_3 is thus formed: —

$$CO_2 + H_2O = H_2CO_3.$$

We also consider that the carbonates, such as calcium carbonate, are derived from this acid. The acid itself, if it exist at all, is very unstable, thus breaking up when liberated: —

$$H_2CO_3 = H_2O + CO_2.$$

The carbonates, however, are very stable and of great importance, and they occur, as previously noted, in immense quantities.

152. Tests for Carbon Dioxide and the Carbonates.—1. The free gas is detected by conducting it through a solution of calcium hydroxide, $Ca(OH)_2$, with which it forms the white precipitate, calcium carbonate, $CaCO_3$.

2. The free gas in water solution may be detected by adding the same solution as before.

3. The carbonates will effervesce with any strong acid, preferably nitric or hydrochloric acids, yielding free carbon dioxide, which may be tested as in 1.

CARBON AND NITROGEN.

CYANOGEN.

153. Cyanogen, CN or Cy, is the only known compound of carbon and nitrogen. It has been isolated; but its constituents do not directly unite to produce it. The cyanogen compounds, as potassium cyanide, KCy, prussic acid, HCy, and other substances containing the group of atoms, CN, are of importance.

Cyanogen gas is prepared by heating mercuric cyanide, $HgCy_2$, in a hard glass test-tube provided with a delivery-tube so arranged that the gas may be collected over mercury. It is soluble in water, and can be condensed at moderate temperature under a pressure of four atmospheres. It possesses an agreeable odor resembling peach blossoms, and burns with a purple flame. This gas is so poisonous that the student should hesitate to experiment with it.

The specific gravity of cyanogen gas is 1.806.

HYDROCYANIC OR PRUSSIC ACID, HCN OR HCY.

154. Prussic Acid is one of the most deadly poisons known. It acts so quickly that antidotes are of little use, though in some cases ammonia and chlorine have been of service in counteracting its effects. It is formed by the decomposition of amygdalin, a complicated substance which occurs in the leaves of some plants, and in the kernels of peach pits, bitter almonds, and other fruits. It can be prepared in a pure, liquid state by passing hydrogen sulphide gas, H_2S, over mercuric cyanide, $HgCy_2$: —

$$HgCy_2 + H_2S = 2\,HCy + HgS.$$

It should be remembered, however, that this acid is a volatile liquid, and that its vapors *are a deadly poison and instantaneously fatal* if inhaled in any considerable quantities. The deadly effects of even dilute hydrocyanic acid may be illustrated by the following experiment which would better by far be omitted: —

EXP. 109 OP. Dissolve 9^g tartaric acid, $C_4H_6O_6$, in 60^{cc} of water; place in a 70^{cc} flask, and add 4^g potassium cyanide, KCy. Shake, and allow to settle, when a dilute solution, containing about 3.6 per cent prussic acid, will be obtained (R. and S.). Administer to a cat about a teaspoonful, and note effects.

The specific gravity of hydrocyanic acid at 18° is 0.6969.

NOTE. See larger manuals for the remaining numerous compounds of cyanogen. The more important cyanides of the metals will be noted under the metals in question; but the student is not to forget that many of them are extremely poisonous.

155. Tests for Hydrocyanic Acid and the Cyanides. — 1. Prussic acid, HCy, when in dilute solution, may be thus detected: To the solution add ammonium sulphide,

NH_4HS, and evaporate nearly to dryness on the water-bath. Ammonium sulphocyanate, NH_4SCy, is formed; this substance, when dissolved in water and treated with ferric chloride, Fe_2Cl_6, turns to a deep-red color.

2. To detect a cyanide in solution, add a few drops of potassium hydroxide, KOH, and then add ferrous sulphate; shake well, and acidify with hydrochloric acid, when prussian blue will be formed if a cyanide be present.

SUG. Use a solution of KCy for these tests.

EXERCISES IN CARBON.

1. Prepare carbon from 10 different articles of food.

2. Write a short description of the carboniferous age in respect to the condition of the atmosphere and vegetation. (Consult some text-book on Geology.)

3. Collect snail shells, clam shells, oyster shells, and a few specimens of limestone, and test for carbonates.

4. PROB. The temperature of the laboratory is 72° F., and the barometer reads 752^{mm}. How many litres of CO_2 gas may be generated from 25^g $CaCO_3$? How many grams of HCl are necessary? How many grams of $CaCl_2$ will be produced?

5. Fill a common clay pipe with walnut, hickory-nut, or butternut meats. Seal the bowl by means of a thick paste of plaster of paris and water. Allow the paste to dry, then heat the bowl in the Bunsen flame. Ignite the gas which soon issues from the stem, and prove that it contains hydrogen and carbon.

SUG. Hold a cold glass tube over the flame. Also hold a piece of cold porcelain against the flame.

6. Produce carbon from marble, snail shells, etc.

7. The value of a sample of coal for reducing iron from its ores is ascertained by making the following *quantitative* determinations: 1. Moisture; 2. Volatile matter; 3. Fixed carbon; 4. Ash; 5. Phosphorus; 6. Sulphur. The first four determinations may be made thus: Place in a weighed porcelain crucible about 5^g of the coarsely-powdered sample, and heat at 100° for several hours. Weigh, and note the loss of weight as "Moisture." Lute on the cover of the crucible by means of a paste of wood ashes, leaving a very small opening in one side. Allow the luting

to dry, and weigh the whole. Now heat to redness for one hour; weigh, and the loss in weight equals the "Volatile matter." The last weight minus the weight of crucible and luting equals the weight of "*Coke.*" Now remove the cover, carefully clean off the luting, and weigh again; then burn the residue in the crucible, and weigh, noting the loss of weight as "Fixed carbon." The last weight minus the weight of crucible equals the "Ash." The value of a coal partly depends upon the amount of fixed carbon it contains. (See Sulphur and Phosphorus.)

8. For valuable information concerning the varieties of coal, coal analysis, etc., see Dana's *System of Mineralogy*, pp. 751–760.

9. As previously stated, it is customary to measure the amount of carbon dioxide as an index to the purity of the atmosphere of a room. This is accomplished by *titration;* and a litre-flask and two reagent solutions are required.

The first solution consists of 5^{g} barium hydroxide, $Ba(OH)_2$, dissolved in 1^{l} of distilled water; the second, 2.863^{g} pure freshly-crystallized oxalic acid, $H_2C_2O_4(H_2O)_2$, in the same amount of water. From the manner of using this latter solution, 1^{cc} corresponds to 1^{mg} carbon dioxide.

The litre-flask is filled, by several puffs of a hand-bellows, with the air to be tested, and the temperature of the room carefully noted. A quantity of the first solution, equal to the space *above* the litre-mark on the neck of the flask, is now added, and the flask vigorously shaken. A portion of the solution in the flask is neutralized, —

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O,$$

and a portion is unchanged. The remainder is now carefully neutralized by means of the second solution, —

$$Ba(OH)_2 + H_2C_2O_4,(H_2O)_2 = BaC_2O_4 + 4\,H_2O,$$

and the number of cubic centimetres is carefully noted; a phenol phthalein solution is employed as an *indicator*. An amount of the first solution equal to that placed in the flask is now directly titrated with the second solution, and the number of cubic centimetres of the latter noted. It is evident that the *difference* between the two numbers thus obtained equals the number of milligrams of CO_2 per litre.

QUERIES. Why do we take 2.863^{g} oxalic acid? Having the number of milligrams CO_2 per litre, multiply the result by 10, and then calculate the number of *cubic centimetres* per 10,000. What principles apply? What is titration? An indicator?

10. The student who wishes to obtain a clearer insight into the processes employed in the Chemistry of the Carbon Compounds, will do well to consult Dr. Remsen's work on that subject.

CHAPTER X.

MOLECULES. — MOLECULAR FORMULAE. — VALENCE.

156. Molecules. — What is meant by the word atom has already been explained. The *chemical atom* is the smallest particle of an element that can take part in chemical reactions. Now, if we consider any chemical compound as, for example, hydrochloric acid, it is clear that the smallest particle of this compound which can be imagined must contain both hydrogen and chlorine, and must contain at least one atom of each of these elements. Such a smallest particle of a compound is called a *molecule.*

The molecules of compound bodies are made up of atoms of different kinds. The molecules of the elements are made of atoms of the same kind. The theory commonly held is that when the elements exist in the free state their atoms unite to form molecules.

The formulae which we use to represent compounds are intended to represent molecules, just as the symbols of the elements are intended to represent atoms. Thus the formulae H_2O, NH_3, HCl, HNO_3, etc., represent the molecules of water, ammonia, hydrochloric and nitric acids; and we see from them that the molecule of water is made up of 2 atoms of hydrogen and 1 of oxygen; that the molecule of ammonia consists of 1 atom of nitrogen and 3 atoms of hydrogen, etc. Knowing the weights of the atoms which make up a molecule, we know the weight of the molecule. It is the sum of the weights of the atoms contained in it. The *molecular weight* of water is 18, which is the sum of the weight of 2 atoms of hydrogen (2 × 1) and of 1 atom of oxygen, 16. The molecular weight of ammonia is 14 (the atomic weight of nitrogen) + 3 (the weight of three atoms of hydrogen) = 17.

QUERY. What is the molecular weight of hydrochloric acid? of nitric acid?

157. Avogadro's Hypothesis. — If the atomic weights of all the elements were known to us there would be little difficulty in determining the molecular formulae of compounds. Thus, if we knew that the atomic weight of oxygen is 16, and on analysis found that water consists of hydrogen and oxygen in the proportion of 1 part of hydrogen to 8 of oxygen, the simplest formula which we could give to the compound would be H_2O, and we might assume that this represents the molecule. A *molecular formula*, according to this, would be nothing more than the simplest formula which could be used to express the composition of a body, assuming the correctness of the commonly accepted atomic weights. In reality, the molecular formulae mean more than this; they are dependent upon a very ingenious and valuable hypothesis, known as the *hypothesis of Avogadro.*

On comparing the specific gravities of a number of gaseous compounds with the molecular weights of the same compounds, it is found that the two sets of figures bear the same relation to each other. In other words, the specific gravity of any compound gas is to the molecular weight of the compound, as the specific gravity of any other gas is to its molecular weight. This leads to the conclusion that *equal volumes of bodies in the form of gas or vapor contain the same number of molecules*, and this is Avogadro's hypothesis. According to the hypothesis, if a cubic inch of hydrochloric acid gas contains (say) 1000 molecules, a cubic inch of any other gas or vapor, measured under the same conditions of pressure and temperature, also contains 1000 molecules. We can not determine the absolute number of molecules present in any given volume, and hence, of course, can not determine the absolute weight of the molecules; but accepting the hypothesis we can easily determine the *relative weights* of molecules of all substances which are gaseous or can be converted into vapor. These relative weights compared to some standard are what we know as the molecular weights.

We may take any simple molecule, as hydrochloric acid, as a standard. The simplest formula which can be assigned to this substance to express its composition is HCl, in which the atomic weight of chlorine is assumed to be 35.5. The molecular weight of a compound of this formula is 36.5. Let this be the standard molecule. The problem now is to determine the weights of the molecules of other bodies in terms of this standard, and in accordance with the principle laid down in Avogadro's hypothesis. We simply determine the relative weights of equal volumes of hydrochloric acid and the other gases or vapors, and, knowing that the molecular weights bear to one another the same relation as these relative weights, the molecular weights can easily be deduced.

The figures which express the relative weights of equal volumes of bodies are called the *specific gravities*. We have then only to compare the specific gravities of gases with that of hydrochloric acid to know the molecular weights of these bodies.

If S' is the specific gravity of hydrochloric acid, and 36.5 its molecular weight; S the specific gravity of some other gas, and M its molecular weight, we have: —

$$S' : 36.5 :: S : M,$$

but S' is known. It is 1.247. Hence we have: —

$$1.247 : 36.5 :: S \text{ (the sp. gr. of any gas)} : M \text{ (its molecular wt.)}.$$

In other words, the relation between the specific gravity of any gas and its molecular weight is represented by a constant quantity which is about 28.8, *i.e.*, —

$$\frac{M}{S} = 28.8, \text{ or } M = 28.8 \times S.$$

The molecular weights of all bodies which can be converted into the form of vapor have been determined by means of this rule, and the molecular formulae are based upon these determinations.

158. Determination of Atomic Weights by means of Avogadro's Hypothesis. — In order to determine atomic weights by means of the hypothesis of Avogadro, we first determine the molecular weights of all compounds which are gaseous or can be converted into vapor. We then analyze these same compounds. On now examining the results of the analysis, we select the smallest quantity of an element which occurs in any of its compounds, as its atomic weight.

The method may be illustrated by taking some of the compounds of carbon as examples.

	Molecular Wt. Found.	Constituents.	
Carbon monoxide	27.96	12 parts C;	16 parts O.
Carbon dioxide	44.16	12 " C;	32 " O.
Marsh gas	16.1	12 " C;	4 " H.
Ethylene	28.0	24 " C;	4 " H.
Acetylene	26.0	24 " C;	2 " H.

The smallest quantity of carbon contained in any of these compounds is represented by the figure 12, and consequently this is accepted as the atomic weight, unless there is some other compound the molecular weight and analysis of which lead us to a smaller figure.

159. Valence.—Having determined the molecular formulae of chemical compounds, we see that they differ markedly from one another. Take, for example, the hydrogen compounds of some of the elements thus far considered. We have hydrochloric acid represented by HCl, water by H_2O, ammonia by H_3N, and marsh gas by H_4C. A fundamental difference between these compounds is noticed in the number of hydrogen atoms contained in each one. In HCl we have 1 H; in H_2O, 2 H; in H_3N, 3 H; and in H_4C, 4 H. The atoms of chlorine, oxygen, nitrogen, and carbon are thus seen to differ from one another in regard to the number of hydrogen atoms which they can hold in combination. The power of any atom to hold a certain number of the simplest atoms in combination is called its *valence.* This term is also applied to the elements. We speak of a *univalent element* meaning an element the atom of which has the power of holding one of the simplest atoms in combination. Thus chlorine and hydrogen are univalent elements.

We may measure the valence of any element by any univalent element with which it will unite. Thus we measure the valence of oxygen by hydrogen. It is *bivalent* because its atom unites with *two atoms of hydrogen.* In the same way we regard nitrogen as *trivalent* because its atom unites with *three atoms of hydrogen;* and carbon as *quadrivalent* because its atom unites with *four atoms of hydrogen.*

Some elements do not unite with hydrogen. In these cases we may measure the valence by means of any other univalent element, as *chlorine.* Thus potassium does not unite with hydrogen, but it does unite with chlorine, forming the compound KCl, which shows that potassium is univalent; calcium forms the compound $CaCl_2$, which shows that calcium is bivalent. The valences of all the elements have thus been determined by a study of the formulae of their compounds. In many cases one and the same element has more than one valence, as shown in the two chlorides of phosphorus, PCl_3 and PCl_5, in the first of which phosphorus appears as a *trivalent* and in the second as a *quinquivalent* element.

160. Substituting Power and Valence. — We have seen that in the formation of salts the hydrogen of the acids is replaced by metals. The number of atoms of hydrogen which the atom of any metal can replace is determined by the valence of the metal. The atom of a univalent metal replaces 1 atom of hydrogen, as is shown in the formation of potassium nitrate, KNO_3, from HNO_3; the atom of a bivalent metal replaces 2 atoms of hydrogen, as in the formation of calcium nitrate, $Ca(NO_3)_2$, from HNO_3, in which case the calcium atom is represented as taking the place of two atoms of hydrogen in two molecules of nitric acid. In barium sulphate, $BaSO_4$, one atom of the bivalent metal barium takes the place of the two hydrogen atoms in sulphuric acid H_2SO_4. In making hydrogen by treating sulphuric acid with zinc, we had another illustration of the replacement of the two hydrogen atoms of sulphuric acid by one atom of the bivalent metal zinc. Numerous illustrations of the different substituting powers of the metals will present themselves when the salts come up for consideration.

NOTE. It is customary to consider the part of an acid which remains in combination with a metal after the hydrogen has been displaced as a group of atoms, and when we wish to take this group more than once, as above, we write $Ca(NO_3)_2$ and not CaN_2O_6. By so doing the formula shows at a glance what acid took part in forming the compound.

EXERCISES IN EQUATIONS.—USEFUL PROBLEMS.

1. The equations previously given might with propriety be termed "Atomic Equations," since they show what we believe takes place at the instant dissociation of a compound occurs.

We may also write "Molecular Equations," showing the state of affairs after all reactions are complete. In order to do this we only need, in addition to what we have already practised, to represent the molecules of the free elements in some appropriate manner, so that the formula for the molecule shall show the number of atoms it contains. It is now becoming customary to do this by the use of subscript figures; thus, O_2, H_2, N_2, P_4, S_2, etc., represent the molecule of oxygen, nitrogen, phosphorus, etc. Let us now again take up some of the atomic equations already given, and rewrite them to represent molecular conditions: —

$K + H_2O = KOH + H$, when rewritten gives $2\,K + 2\,H_2O = 2\,KOH + H_2$,
$Zn + H_2SO_4 = ZnSO_4 + 2\,H$ becomes $Zn + H_2SO_4 = ZnSO_4 + H_2$;
$2\,P + 5\,O = P_2O_5$ becomes $2\,P_4 + 10\,O_2 = 4\,P_2O_5$;
$S + 2\,O = SO_2$ becomes $S_2 + 2\,O_2 = 2\,SO_2$.

By inspecting the equations thus rewritten it becomes apparent that molecular equations are somewhat the more complex of the two, and that to write them properly requires a knowledge of the molecular formulae of the elements. In the compounds, as previously stated, the formula also represents the molecule; not so however with the symbols of the elements; and since it is first necessary to determine the *vapor density* of an element before we can determine its molecular formula, it is evident that when we come to solids not readily volatilized it is manifestly absurd to write such a formula as Au_2, Pt_3, etc., especially if we agree to represent the molecules of elements by subscript figures.

Write in molecular formulae: —

$$\begin{aligned} KClO_3 &= KCl + 3O; \\ Na + H_2O &= NaOH + H; \\ C + 2O &= CO_2; \\ 3Fe + 4O &= Fe_3O_4; \\ Zn + O &= ZnO. \end{aligned}$$

2. To calculate the weight of a given volume of any gas from its molecular weight: —

Prob. 1. How much does 1^l of HCl gas weigh at 0°?

Solution. The molecular weight equals $35.5 + 1 = 36.5$, and the *density* (with reference to H) equals $36.5 \div 2 = 18.25$. Now 1^l of H at 0° and 760^{mm} weighs 0.0896^g, and it is evident that the required weight equals 18.25×0.0896. In case the temperature and pressure vary from standard conditions the problem may be finished by Art. 87.

Note. Note that *The density of a gas* ($H = 1$) *equals one-half its molecular weight.* This follows from the fact that we take the hydrogen molecule, H_2, as 2; or the half molecule, H, as unity.

Prob. 2. How much do 6^l of chlorine weigh at 15° and 750^{mm}?

Sug. The molecular formula of chlorine is Cl_2, and its density equals $2 \times 35.5 \div 2 = 35.5$ or the atomic weight of Cl. We may here note that the *density* and *atomic weights* of the gaseous elements are numerically equal.

Prob. 3. Compute the weights of 1^l of the following gases: O, N, N_2O, N_2O_3, NH_3, H_2S, SO_2, CO_2, CO.

3. To compute the specific gravity (air = 1) of a gas *from its molecular weight.* Divide the weight of 1^l of that gas by the weight of 1^l of air, or 1.293.

Prob. 4. What is the specific gravity of CO_2? H_2S? CO? NH_3?

4. Show that one needs simply to remember the atomic weights of the elements to compute: 1. The molecular weight of any gas; 2. Its density; 3. The weight of 1^l.

CHAPTER XI.

SULPHUR.—SELENIUM AND TELLURIUM.—THEIR OCCURRENCE, PREPARATION, TESTS, ETC.

SULPHUR.

SYMBOL, S''.—ATOMIC WEIGHT, 32.—SPECIFIC GRAVITY (CRYSTALS), 2.05.

161. **Occurrence.**—Sulphur occurs native in volcanic regions, and in its compounds with other elements it is widely distributed. The most plentiful of these compounds are the sulphides, iron pyrites, FeS_2, or Fool's Gold; galena, PbS; cinnabar, HgS; and the sulphates, gypsum, $CaSO_4 + 2\,H_2O$; heavy spar, $BaSO_4$; green vitriol or ferrous sulphate, $FeSO_4 + 7\,H_2O$, etc.

Native sulphur occurs in regular, yellowish, transparent, octahedral crystals, and in other forms derived from this primary crystal. It is also found in a massive state being then known as volcanic sulphur.

162. **Preparation.**—Since sulphur in its various forms is a common article of commerce it may readily be procured for class purposes. The common roll sulphur or *brimstone* is prepared by distilling the crude ore in large earthen-ware retorts, and condensing the vapors in stoneware condensers. More frequently, however, it is obtained by building up the crude ore in the form of a kiln

or charcoal pit, where the ore is roasted by burning a portion of the sulphur as a fuel. The sulphur is melted from its accompanying impurities, and runs down into a receptacle prepared to receive it at the bottom of the pit.

It is afterwards purified by distillation, and cast into the ordinary rolls or sticks.

Flowers of Sulphur, also an article of commerce, are obtained by vaporizing a quantity of sulphur and bringing the vapor into a cold condenser, where this variety is produced in a manner analogous to snow.

Exp. 110 p. Dissolve 2^g flowers of sulphur in 13^{cc} of water, to which has been added 1^g slacked lime (prepared by treating 1 part quicklime with 3 parts water). The product calcium pentasulphide, CaS_5, is formed. Write the equation. Now add to the solution hydrochloric acid, when the liquid turns white, very finely divided sulphur being obtained.

The substance thus prepared is an article of commerce known as *lac sulphuris* or milk of sulphur.

163. Properties. — Exp. 111 p. Dissolve 1^g sulphur in 3^g carbon bisulphide, CS_2. Place the solution in a beaker glass, and allow it to evaporate, without heat, in the atmosphere. Octahedral sulphur crystals will be obtained. Allow these crystals to stand for several days, noting from time to time any changes that may occur.

Sulphur crystals occur in no less than thirty different forms all derived from the primary octahedron. The specific gravity of these primary crystals at 0° is 2.05.

Exp. 112 t. Melt in an evaporating dish 100^g sulphur and heat to 230°, when the molten mass will turn black. Now pour into a basin of cold water, and when cold remove and examine the product obtained. Leave for several days in the water, and occasionally observe what changes occur.

The modification of sulphur thus obtained is known as *plastic sulphur*, and at first strongly resembles caoutchouc, in that it is elastic; it soon becomes brittle, however, upon standing. The specific gravity of this form is 1.96.

Exp. 113 T. Melt in a sand crucible a quantity of sulphur and allow it to cool slowly. When a crust forms over the surface of the molten sulphur make an opening through the crust and pour off the liquid portion. Note the peculiar needle-shaped crystals attached to the solid crust.

QUERIES. How many different forms or modifications of sulphur have you observed? What changes take place in the crystals last obtained when they are allowed to stand?

Sulphur is extensively used in making sulphuric acid and in the manufacture of rubber goods. When heated at moderate temperatures with crude rubber gum, 2 to 3 per cent of sulphur is absorbed, and the product obtained is firmer and better adapted to some industrial requirements than the pure gum itself. When the temperature is raised to a higher degree the substance called *vulcanite* or *ebonite* is obtained.

QUERY. What developments in the rubber industry are due to Charles Goodyear?

Exp. 114 P. Dip into powdered sulphur a pine splinter and ignite; note the flame and the odor emitted. What does the odor resemble? The fumes have the formula SO_2. Write the equation.

Sulphur is used in the manufacture of matches and is burned for bleaching straw goods. Some forms are also employed in medicine.

It is capable of uniting directly with most metals to form sulphides.

164. Tests for Free Sulphur. — 1. Free sulphur is distinguished, if in considerable quantities, by its physical properties, and by its flame and the odor of its fumes.

2. If the quantity be too small to test as in 1, fuse it on platinum foil with sodium carbonate, Na_2CO_3; then place the fused mass, which is sodium sulphide, Na_2S, on a bright piece of silver, and moisten with a drop of water. If free sulphur be present, a black spot of silver sulphide will be obtained.

CAUTION. The Na_2CO_3 and charcoal must be free from sulphur; likewise the illuminating gas used for the blow-pipe flame. The alcohol lamp is best to use for this test.

NOTE. Since sulphur blackens silver, egg spoons, mustard spoons, etc. are gilt to prevent their tarnishing. Silver ware blackened by sulphur is easily brightened by washing in a solution of potassium cyanide, KCy; this is better than scouring, since the cyanide does not attack the pure silver. How may the black spot obtained in 2 be removed?

SULPHUR AND HYDROGEN.

165. Sulphur and hydrogen form two compounds, viz.: —

Hydrogen Sulphide, H_2S,
Hydrogen Persulphide, H_2S_2(?).

Of these the first alone is of importance to the beginner.

HYDROGEN SULPHIDE.

166. Occurrence. — Hydrogen sulphide, commonly known as *sulphuretted hydrogen*, is of wide occurrence, both free and combined. The waters of many famous "sulphur springs" contain this gas in large quantities. It is a product of volcanic action and of the decomposition of albuminous substances; thus the peculiar odor of rotten eggs is partly due to the hydrogen sulphide evolved.

The sulphides, which may be regarded as derived from this acid, are found in great abundance, as already mentioned.

167. **Preparation.** — Exp. 115 p. Place in a test-tube a small quantity of water, say 10^{cc}, and add a small piece of ferrous sulphide, FeS; now add 1^{cc} of sulphuric acid, and close the tube quickly with a perforated cork containing a glass U-shaped jet delivery-tube. The gas will soon issue through the jet, when it may be ignited. Note the odor, but do not allow more gas than is necessary to escape, since it is somewhat poisonous. The contents of the tube should be poured into the sink as soon as a sufficient amount of gas has been obtained, but in case a considerable piece of the sulphide remains this may be saved for further use.

This is the general method and the one almost exclusively employed in laboratory practice for the production of hydrogen sulphide. The chemist thus produces it for analytical purposes, as will subsequently be explained. It is well to have a gas chamber wherein this gas may be produced and wherein the whole contents of the test-tube may be retained, since another reagent, ferrous sulphate, is thus produced: —

$$FeS + H_2SO_4 = H_2S + FeSO_4.$$

This latter compound may be separated by crystallization.

In case large quantities of sulphuretted hydrogen are required, a generating flask may be employed instead of a test-tube, and the gas may be washed through warm water. An aqueous solution in cold water is to be had, but the gas itself, freshly generated, is preferable for qualitative work.

Hydrogen sulphide is also formed by the action of some of the other acids on the sulphides; by burning sulphur in an atmosphere of hydrogen; by passing hydrogen through boiling sulphur, and by heating paraffine with sulphur. All these methods are, for various reasons, not well adapted for obtaining the gas in practice.

168. Properties. — Hydrogen sulphide is a colorless, inflammable gas, possessing a disagreeable odor somewhat resembling rotten eggs. It is condensed, at ordinary temperatures under a pressure of 17 atmospheres, to a colorless liquid which boils at −61.8° and freezes at −85°. Its specific gravity at 0° is 1.191, and 1^l weighs 1.522^g. 1^{cc} of water at 0° absorbs about 4.4^{cc} hydrogen sulphide, forming a slightly acid solution.

Exp. 116 P. Place in several different test-tubes solutions of metallic salts, such as copper sulphate, $CuSO_4$; mercuric chloride, $HgCl_2$; lead acetate, $Pb(C_2H_3O_2)_2$, and silver nitrate, $AgNO_3$. Generate hydrogen sulphide as in Exp. 115, and successively place the jet into these solutions, allowing the gas to bubble up through them. Precipitates which are respectively the sulphides of the different metals will be formed.

It is thus that the chemist employs hydrogen sulphide in analytical operations, and the great utility of this gas becomes apparent when it is known that by its aid the metals may be separated into groups. In short, it is another group reagent (p. 98). The same is true of one of its compounds, ammonium sulphide, $(NH_4)_2S$.

Sug. Try the effect of H_2S upon solutions of arsenic, antimony, cadmium, copper, and tin. Note the colors of the precipitates.

Exp. 117 P. Pass sulphuretted hydrogen through nitric acid; aqua regia; strong hydrochloric acid; sulphuric acid. Do you obtain *precipitates?* If so, collect and burn on a pine splinter. Note the odor of the fumes. What is the sediment obtained? What effect do stronger acids have upon hydrogen sulphide? Make a solution of lead nitrate, $Pb(NO_3)_2$, and strongly acidify with nitro-hydrochloric acid. Now pass hydrogen sulphide. Do you obtain lead sulphide? Why?

169. **Tests for the Sulphides.** — 1. Free hydrogen sulphide in quantity is distinguished by its odor and by its blackening effect upon paper moistened with lead acetate, $Pb(C_2H_3O_2)_2$. Also see Exp. 38.

2. A sulphide, when fused on platinum foil or a bit of porcelain, — as a piece of broken evaporating dish, — with sodium carbonate, and moistened, produces a black spot when placed on a clean piece of silver.

QUERIES. How do the sulphides, as FeS, behave with sulphuric acid? What is meant by a *test?*

NOTE. The salts of easily reducible metals, such as those of lead and mercury, must not be fused on platinum, since these metals form with the platinum alloys which are fusible at high temperatures. The platinum may thus be ruined. In such cases it is necessary to fuse on charcoal or porcelain. What disadvantage does this latter process involve?

HYDROGEN PERSULPHIDE, H_2S_2(?).

170. Hydrogen persulphide may be prepared by boiling (say) 1^g slacked lime with 16^{cc} water and 2^g flowers of sulphur. The cold clear solution is then poured into dilute hydrochloric acid, when the persulphide falls to the bottom of the vessel as an oily liquid.

It has a very disagreeable odor, more pungent than that of hydrogen sulphide. It is not important for the beginner.

SULPHUR AND OXYGEN.

171. There are two oxides of sulphur deserving special mention, viz.: —

Sulphur Dioxide, SO_2,
and Sulphur Trioxide, SO_3.

These oxides are respectively the anhydrides of sulphurous and sulphuric acids. The manner in which they combine with a molecule of water is worthy of notice: —

1. $H_2O + SO_2 = H_2SO_3$;
2. $H_2O + SO_3 = H_2SO_4$.

It will be seen that in either case one molecule of water and one molecule of oxide form but *one* molecule of acid. In the case of the oxacids of nitrogen, bromine, chlorine, and iodine *two* molecules of acid were thus formed.

Two other oxides corresponding to the formulae, S_2O_3 and S_2O_7, are known.

SULPHUR DIOXIDE, SO_2.

172. Occurrence. — This oxide is the gas formed when sulphur is burned in the atmosphere. It occurs free in volcanic gases, and combined with other elements, as in the *sulphites* or salts of sulphurous acid.

173. Preparation. — EXP. 118 P. Place in a generating flask fitted with a delivery-tube 1^g very fine copper filings and 6^{cc} strong sulphuric acid. Heat until a gas begins to escape. Note the odor, and collect by displacement in a large test-tube, or small, tall jar.

SUG. Some other metals when thus treated also yield sulphur dioxide. Try several, such as iron, mercury, and lead.

When sulphur dioxide is thus prepared the reaction may be indicated by the equation: —

$$Cu + 2\,H_2SO_4 = CuSO_4 + 2\,H_2O + SO_2.$$

Notice the difference between this reaction and that which takes place when sulphuric acid and zinc are brought together. In the latter case the reaction is represented thus: —

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

Whenever a metal reacts with an acid the first action consists in the replacement of the hydrogen of the acid by the metal. The hydrogen is liberated and a salt is formed. In the case of copper and sulphuric acid, however, the reaction does not take place at ordinary temperatures, and at higher temperatures the hydrogen which is first liberated acts upon the sulphuric acid reducing it to sulphur dioxide: —

$$H_2SO_4 + H_2 = 2\,H_2O + SO_2.$$

A common method of preparing this gas is to burn sulphur in the air. Many other methods are also known, such as heating sulphur and carbon with sulphuric acid, roasting pyrites, etc.

174. Properties. — Sulphur dioxide gas is easily condensed by passing it through a spiral glass tube surrounded by a freezing mixture. It is very soluble in water, 1^{cc} of which dissolves, at 0°, about 79.8^{cc} of this gas. Its specific gravity is 2.211, and 1^{l} weighs 2.862^{g}. It condenses at $+59°$ under 79 atmospheres and boils at $-8°$ under 1 atmosphere.

Sulphur dioxide is used in great quantities for preparing sulphuric acid, in which case it is prepared by burning sulphur or iron pyrites in a current of air.

Exp. 119 p. Suspend in a jar of sulphur dioxide a strip of moistened unbleached silk; a moist wheat straw; a piece of white woollen yarn.

Sulphur dioxide is used for bleaching such goods as chlorine would injure. It produces its effects by *reduction* instead of oxidation, as in the case of those bleaching reagents previously noticed. It unites with the oxygen of water, liberating hydrogen, and this latter gas enters into combination with the coloring matter to form colorless compounds.

Queries. How do milliners prepare the sulphur dioxide which they use in bleaching straw goods? What other substances have been mentioned as reducing agents? What is meant by *reduction?*

A solution of sulphur dioxide in water becomes oxidized if it comes in contact with air, sulphuric acid being formed. It is probable that in the solution sulphurous acid, H_2SO_3, is present, and that this takes up oxygen, thus passing into sulphuric acid. Write the equations.

Sulphur dioxide is also a good disinfectant, and will prevent the decay of meats and vegetables when applied for that purpose. It also prevents fermentation.

175. Tests for Sulphur Dioxide.—1. Its odor is marked and well known, resembling that of burning matches.

2. Suspend in this gas a strip of paper which has been dipped into a solution of starch paste and potassium iodate, KIO_3. Iodine is liberated, and the paper becomes blue:—

$$2\,KIO_3 + 5\,SO_2 + 4\,H_2O = 2\,HKSO_4 + 3\,H_2SO_4 + I_2.$$

Note. The sulphur dioxide must not be present in excess, or the paper will be bleached, hydriodic acid being produced. Write the equation.

Sulphur Trioxide, SO_3.

176. Sulphur trioxide is somewhat difficult of preparation and very unstable owing to the eagerness with which it unites with water.

It is prepared for commerce by passing sulphur dioxide together with oxygen over finely divided platinum in a highly-heated porcelain tube. It may also be prepared by heating strong sulphuric acid with phosphorus pentoxide:

$$H_2SO_4 + P_2O_5 = 2\,HPO_3 + SO_3.$$

Sulphur trioxide was formerly supposed to be the true sulphuric acid, but as soon as it was separated it proved to be a white crystalline solid without action upon the metals in absence of moisture. The discovery of this substance brought about a marked change in the views held in regard to salts and acids, and was one of the many causes which have led up to our present conceptions concerning chemical reactions and chemical formulae.

THE SULPHUR OXACIDS.

177. In this series eight different acids are known, the names and formulae of which are shown by the subjoined list:—

Hyposulphurous acid . . .	H_2SO_2;
Sulphurous acid	H_2SO_3;
Sulphuric acid	H_2SO_4;
Thiosulphuric acid	$H_2S_2O_3$;
Dithionic acid	$H_2S_2O_6$;
Trithionic acid	$H_2S_3O_6$;
Tetrathionic acid	$H_2S_4O_6$;
Pentathionic acid	$H_2S_5O_6$?

Note. The root "thion" is of Greek derivation, signifying sulphur.

By inspection, it will be seen that all these acids are dibasic, possessing two atoms of replaceable hydrogen; hence, they yield both acid and normal salts, *e.g.*, monosodium sulphite, $HNaSO_3$; sodium sulphite, Na_2SO_3, etc.

Acids which contain but one replaceable hydrogen atom are called *monobasic acids;* those which contain two replaceable hydrogens are called *bibasic acids;* those with three are called *tribasic acids*, and those which contain four are called *tetrabasic acids.* Most common acids belong to the first two classes. All the acids previously considered, excepting carbonic acid, are monobasic; the latter and the sulphur acids are bibasic. The principal tribasic acid is phosphoric acid, H_3PO_4. There is no common tetrabasic acid.

SUG. Name the salts formed by the sulphur acids and potassium. Write their formulae.

NOTE. The student who has thus far followed these pages will have noted that the rarer acids are chiefly of interest to the scientist, and that they are all unstable and somewhat difficult of preparation. His experience, moreover, with these unimportant compounds will have served to give him a sufficient conception as to the characteristics of the class of substances to which they belong. We shall therefore note but three acids of this series; viz., sulphurous, sulphuric, and thiosulphuric acids.

SULPHUROUS ACID, H_2SO_3.

178. This acid, as previously noted, is formed when sulphur dioxide is passed into water. It is an unstable acid constantly giving off sulphur dioxide fumes; but the sulphites are a well known class of salts.

EXP. 120 P. Pass sulphur dioxide gas into a test-tube of cold water; also into a cold solution of sodium or potassium hydroxide. What does each tube contain after passing the gas? Gently evaporate to dryness the contents of the second tube, and a salt is obtained. Complete this equation, —

$$H_2O + SO_2 + KOH = \ . \ . \ .$$

Use the contents of these tubes for the following: —

179. Tests for Sulphurous Acid and the Sulphites. — 1. Free sulphurous acid in quantity is recognizable by its odor.

2. In traces it may be detected by a solution of starch paste and potassium iodate, owing to the blue tinge produced. It will also blacken a strip of paper moistened with silver nitrate.

3. The sulphites in solution upon addition of a stronger acid (HCl, H_2SO_4) remain clear, yielding sulphur dioxide fumes. (See Thiosulphuric Acid.)

4. When barium chloride is added to a solution of a sulphite, the white precipitate barium sulphite, $BaSO_3$, is thrown down. Divide this precipitate in two parts: to the first add hydrochloric acid; it is soluble. To the second add nitric acid; the sulphite is oxidized to barium sulphate, $BaSO_4$, a white precipitate insoluble in acids.

Sug. Complete and balance the following equations, and explain the principles they illustrate: —

$$\begin{aligned}
5H_2SO_3 + 2KIO_3 &= I + HKSO_4 + H_2SO_4 + \ . \ . \ .; \\
Na_2SO_3 + HCl &= SO_2 + \ . \ . \ . + NaCl; \\
Na_2SO_3 + BaCl_2 &= NaCl + \ . \ . \ .; \\
BaSO_3 + HNO_3 &= BaSO_4 + H_2O + \ . \ . \ .
\end{aligned}$$

Sulphuric Acid, H_2SO_4

180. Occurrence. — Although sulphuric acid does not occur in nature except in volcanic waters, it is the most important acid known to the chemist and to commerce.

It has even been stated that the prosperity of a country may be estimated by the amount of sulphuric acid which that country consumes.

Its salts are very stable and of great value, as, for example, blue vitriol, $CuSO_4 + 5 H_2O$, a salt of copper used for galvanic batteries and many other purposes; gypsum or land plaster, $CaSO_4 + 2 H_2O$, used by farmers as a manure; green vitriol or ferrous sulphate, $FeSO_4 + 7 H_2O$, a well-known salt used in the laboratory as a reagent, and also used for purifying water-closets, sewers, etc.; Glauber salts, $Na_2SO_4 + 10 H_2O$; Epsom salts, $MgSO_4 + 7 H_2O$, and the sulphates of the alkaloids used in medicine.

181. Preparation. — Exp. 121 t. Although the student will have this acid upon his table, where he may study its properties at his leisure, it might be well to illustrate the interesting process of its manufacture. The formation of sulphuric acid may be beautifully shown by employing the apparatus illustrated in Fig. 18. G is a glass globe used as a condensing chamber. B is a generator containing copper filings and

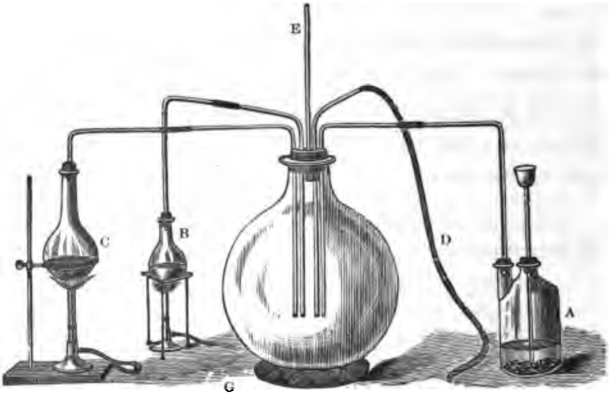

Fig. 18.

sulphuric acid for the purpose of producing sulphur dioxide. C is a flask containing water for generating steam. A contains copper filings and nitric acid for generating nitrogen dioxide and nitrogen trioxide. D is used to convey air into the condensing chamber, and is attached to a hand-bellows. E is an escape-pipe to allow the waste gases, nitrogen and nitrogen dioxide, etc., to be forced out of the chamber. In practice most of these gases are utilized, but in this experiment E must be placed in a good ventilating draft. When the products of A, B, and C begin to fill the condenser, a steady, but gentle, current of air from the bellows must be forced through G until the close of the experiment. Sulphuric acid is thus produced, and falls to the bottom of the condenser.

In preparing commercial sulphuric acid the materials and principles used vary but slightly from those illustrated in the foregoing experiment. The sulphur dioxide is prepared by burning sulphur or roasting iron pyrites, FeS_2, in a current of air. The fumes are conducted into immense lead-lined chambers where they are mixed with air and steam and the higher oxides of nitrogen, as N_2O_3 and NO_2; or at first a little nitric acid formed from sodium nitrate and sulphuric acid is used. The steam is obtained from a boiler and is blown into the chamber through jets stationed at different points.

The chemical processes involved in the manufacture of sulphuric acid are quite complicated. The essential features will appear from the following brief description: When the sulphur dioxide and nitric acid first come together in the presence of steam this reaction takes place: —

$$2\,HNO_3 + 3\,SO_2 + 2\,H_2O = 3\,H_2SO_4 + 2\,NO.$$

As will be seen, the nitric acid is reduced to nitric oxide, NO, and this is incapable of oxidizing any more sulphur dioxide; but the oxygen of the air which is present immediately transforms the nitric oxide into nitrogen tetroxide, NO_2 ($NO + O = NO_2$), and this, in the presence of steam, converts a further quantity of sulphur dioxide into sulphuric acid, as indicated in this equation: —

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO,$$

and is itself again reduced to nitric oxide. This NO again takes up oxygen to form nitrogen tetroxide, which in turn oxidizes sulphur dioxide, and so on, indefinitely. Thus, theoretically, starting with a small quantity of nitric acid, an infinite quantity of sulphur dioxide could be converted into sulphuric acid, as, after the nitric oxide, NO, is once formed, it simply serves the purpose of transferring oxygen from the air to the sulphur dioxide. Practically, of course, there is always some loss of the oxides of nitrogen, and this loss must be made good by a fresh supply in order to make the operation continuous.

The acid formed in the leaden chambers is a weak acid having a specific gravity of 1.55. It is withdrawn into large leaden pans, and concentrated until its specific gravity reaches 1.71, when it is quickly removed, since any further concentration would result in the destruction of the pan.

It is further concentrated and purified in glass or platinum stills until its specific gravity becomes 1.84, when it is ready for the market.

182. Properties. — Commercial sulphuric acid has an oily appearance, and was formerly prepared by distilling green vitriol or ferrous sulphate: owing to these facts it received the name *oil of vitriol.*

When exposed to the atmosphere it soon absorbs moisture, thereby becoming dilute. In consequence of its great hygroscopic power, it is employed under the receiver of the air-pump to aid in concentrating aqueous solutions of such substances as would not bear heating without undergoing decomposition. Pumice stone moistened with sulphuric acid is used to dry those gases upon which the acid has no action. The pure acid may also be used in a wash-bottle.

Queries. For which gases already considered may it be used? For which ones should it not be used?

When sulphuric acid is brought together with water in quantities proportional to their molecular weights, the *hydrate* of sulphuric acid, $H_2SO_4 + H_2O$, is formed.

When this acid mixes with water much heat is evolved. In diluting it with water it is best slowly to add the acid to the water, and not the water to the acid, otherwise the vessel containing the acid may be broken and a serious accident ensue.

Exp. 122. Try the effect of strong sulphuric acid upon a splinter of wood; a bit of cloth; a lump of sugar. What occurs?

Sulphuric acid chars vegetable substances by abstracting water, or the elements of water, hydrogen and oxygen.

In its industrial uses, sulphuric acid is employed very extensively in the manufacture of soda (sodium carbonate, Na_2CO_3), artificial fertilizers, nitroglycerine, etc., and in the refining of petroleum.

Query. For what purposes has sulphuric acid thus far been employed in the laboratory?

183. Tests for Sulphuric Acid and the Sulphates. — 1. Sulphuric acid or a soluble sulphate may be detected by adding to the solution barium chloride, $BaCl_2$, when the white precipitate, barium sulphate, $BaSO_4$, is obtained.

This precipitate is insoluble in acids.

2. An insoluble sulphate may be fused on platinum foil or a bit of porcelain with sodium carbonate; the moistened residue produces no spot on silver. If fused in the same way on charcoal a spot will be produced.

QUERIES. If a sulphate, when treated on charcoal with sodium carbonate, yields sodium sulphide, Na_2S, what action upon the acid has occurred? If the black spot on silver be Ag_2S, what other compound is probably formed in the reaction: —

$$2\,Ag + Na_2S = Ag_2S + \ldots ?$$

(SUG. H and O are present in H_2O to unite with Na.) Write this equation in full, and balance. How can you distinguish a sulphate from a sulphide, by fusing, etc.?

NORDHAUSEN, OR FUMING SULPHURIC ACID, $H_2S_2O_7$.

184. This acid is made by heating dried ferrous sulphate which still contains a little moisture. The reaction is represented thus: —

$$4\,FeSO_4 + H_2O = 2\,Fe_2O_3 + 2\,SO_2 + H_2S_2O_7.$$

It may also be made by passing sulphur trioxide, SO_3, into strong sulphuric acid: —

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

It breaks up readily, forming sulphur trioxide and sulphuric acid. When a vessel containing it is opened, fumes of the trioxide escape; hence it is called *fuming sulphuric acid.*

Water acts violently upon it, converting it into ordinary sulphuric acid: —

$$H_2S_2O_7 + H_2O = 2\,H_2SO_4.$$

The principal uses of this acid are for dissolving indigo in the process of dyeing Saxony blue and for manufacturing the coal-tar colors.

QUERY. Since $H_2S_2O_7 = H_2SO_4 + SO_3$, should this acid be regarded as a distinct acid or as a solution of SO_3 in H_2SO_4?

THIOSULPHURIC ACID, $H_2S_2O_3$.

185. This acid, in a free state, is so unstable that its existence is somewhat problematical; but its salts, the thiosulphates, are well-known articles of commerce. The principal one, sodium thiosulphate, $Na_2S_2O_3$, is used by photographers as a solvent for the unchanged silver salts in their prints, which are thus "fixed," as the process is termed. This salt is formed by fusing sodium sulphite with flowers of sulphur, thus: —

$$Na_2SO_3 + S = Na_2S_2O_3.$$

When a thiosulphate in a hot solution is treated with hydrochloric acid or sulphuric acid, free sulphur is deposited, and sulphur dioxide fumes evolved, thus: —

$$Na_2S_2O_3 + 2\,HCl = 2\,NaCl + S + SO_2 + H_2O.$$

QUERY. How does a sulphite behave with hydrochloric acid?

NOTE. This sulphur acid was formerly known as hyposulphurous acid, and its salts as hyposulphites; while the acid of the formula H_2SO_2 was called hydrosulphurous acid, and its salts hydrosulphites. Sodium thiosulphate is still commonly known to druggists as hyposulphite of sodium.

186. Tests for the Thiosulphates. — 1. With hydrochloric acid their solutions yield a precipitate of sulphur, and give off sulphur dioxide fumes.

2. Barium chloride, when added to a solution of a thiosulphate, yields a white precipitate soluble in hydrochloric acid, but leaving a residue of sulphur.

187. To distinguish between the Soluble Salts of the Sulphur Acids. — The solution may contain a sulphide, a sulphite, a sulphate, or a thiosulphate. There are many ways of making this distinction, one of which is as follows: —

1. Evaporate a portion of the solution to dryness, and fuse on charcoal with sodium carbonate, etc. A black spot on silver indicates *any* of these acids. Then fuse on porcelain, etc.; no spot indicates a *sulphate.*

2. To a portion of the solution add silver nitrate, $AgNO_3$: —

(*a*) A black precipitate formed at once indicates a *sulphide.*

(*b*) No precipitate indicates a *sulphate.*

(*c*) A white precipitate, obtained by adding a single drop of the silver nitrate, and which does not dissolve upon shaking, indicates a *sulphite.* This precipitate, upon standing, or upon being heated, turns black, metallic silver being the final product obtained.

(*d*) A white precipitate from a single drop of the nitrate, which dissolves upon shaking, indicates a *thiosulphate.* Add an excess of nitrate, and boil. A black precipitate, Ag_2S, is finally obtained.

(*e*) If the student is still in doubt as to whether the solution contains a sulphite or a thiosulphate, add hydrochloric acid to a fresh portion of the solution; sulphur dioxide fumes from a clear solution indicate a *sulphite;* the same fumes from a clouded solution indicate a *thiosulphate.*

SUG. Try to distinguish these acids by means of barium chloride, $BaCl_2$, etc.

SULPHUR AND CARBON.

188. Carbon Bisulphide, CS_2, is the only known compound of sulphur and carbon. This is a colorless, inflammable, highly refracting liquid, boiling at +46°, and possessing a specific gravity of 1.292. It has a powerful odor, in its impure commercial forms, and its fumes are poisonous; when pure it has a pleasant, ethereal odor.

It is prepared by passing the vapor of sulphur through a cylinder heated to redness and containing charcoal.

Carbon bisulphide is employed for a variety of purposes. In the laboratory it is used as a solvent for bromine and iodine, as we have previously seen; in the manufactures it is employed as a solvent for various gums, such as rubber gum; shoemakers mend shoes with a cement made by dissolving crude rubber in carbon bisulphide; in woollen manufacture it is used to regain the oils with which the wool is treated during some of the necessary processes; in optics the hollow prisms used for decomposing light, and for spectrum analysis, are filled with carbon bisulphide; in agriculture it is employed as an insecticide, and (in the form of salts) in combating the phylloxera. It is also said to be of value in exterminating woodchucks and other burrowing animals, for which purpose it is placed in their burrows, which are then tightly closed with earth.

The odor of carbon bisulphide betrays its presence, and serves as a *test*.

SELENIUM.

SYMBOL, SE″. — ATOMIC WEIGHT, 79. — SPECIFIC GRAVITY (CRYSTALLINE), 4.3.

189. Occurrence. — Selenium is a rare element closely resembling sulphur. It was discovered in 1817 by Berzelius while examining the deposits of the sulphuric acid chambers at Gripsholm. It does not occur native, but is found in the selenides, such as lead selenide, PbSe, and the double selenides of mercury, lead, silver, and copper.

190. Preparation. — Owing to the rarity of this element, the student will probably do no work with it, therefore general processes alone will be briefly given.

The residue of the sulphuric acid chambers is mixed with potassium nitrate and then thrown into a red-hot crucible, where it deflagrates, forming potassium selenate, K_2SeO_4, which is now contaminated with many impurities contained in the chamber residue. This impure mass is now digested with hydrochloric acid, and the solution filtered and evaporated nearly to dryness, selenious acid, H_2SeO_3, being formed. This acid is then treated with sulphurous acid, thus: —

$$H_2SeO_3 + 2\,H_2SO_3 = 2\,H_2SO_4 + H_2O + Se.$$

The finely divided selenium thus produced is separated by filtration.

191. Properties. — Finely divided selenium when viewed by transmitted light has a reddish color. In its properties and compounds it resembles sulphur. It is known in three modifications; viz., amorphous, vitreous, and crystalline. Flowers of selenium, a scarlet powder, is obtained in a manner similar to flowers of sulphur.

The specific gravity of selenium varies from 4.5 to 4.8.

192. Selenium Compounds. — 1. Selenium and hydrogen form *hydrogen selenide*, H_2Se, a poisonous gas obtained by the direct union of the vapor of selenium with hydrogen, or by treating potassium selenide with hydrochloric acid.

2. Selenium and oxygen form *selenium dioxide*, SeO_2, when the former is burned in a current of the latter, or by treating the former with strong nitric acid.

Selenium dioxide and water form *selenious acid*, H_2SeO_3, from which the selenites may be derived. Selenium dioxide has the odor of rotten cabbage or horseradish.

3. *Selenic acid*, H_2SeO_4, is obtained by passing a stream of chlorine gas through water in which finely divided selenium is suspended, thus: —

$$Se + 3\,Cl_2 + 4\,H_2O = 6\,HCl + H_2SeO_4.$$

This acid forms salts called selenates.

193. Tests for Selenium and its Compounds. — 1. Free selenium burned in the air gives the odor of the dioxide.

2. Hydrogen selenide is distinguished by its very offensive odor. It causes inflammation of the eyes and seriously affects the lining membranes of the nose.

3. The selenides when heated on charcoal give the dioxide fumes; when fused with potassium nitrate, and when the solution of the residue in hydrochloric acid is treated with sulphur dioxide, they yield free selenium.

4. The selenites when heated on charcoal also give the fumes of burning selenium; their solutions with sulphur dioxide yield free selenium.

5. The selenates, with sulphur dioxide, yield free selenium when acidulated with hydrochloric acid. The fumes of a selenate heated on charcoal are also those of the dioxide.

TELLURIUM.

SYMBOL, Te''. — ATOMIC WEIGHT, 128.? — SPECIFIC GRAVITY, 6.24.

194. Occurrence. — Tellurium is a rare element which occurs native in small quantities and in combination with certain metals, as tellurides, particularly with gold, silver, lead, and bismuth.

195. Preparation. — Tellurium is prepared by mixing bismuth telluride (which also contains some sulphur as an impurity) with sodium carbonate and oil; this mixture is rubbed to a paste, placed in a closed crucible, and strongly heated. The mass is then lixiviated with water, when a solution of sodium telluride and sulphide is obtained. Upon exposure to light and air tellurium, in the form of gray powder, is deposited in this solution; this powder is purified by distilling it in an atmosphere of hydrogen.

196. Properties. — Tellurium is a very brittle, bluish-white solid, possessing a metallic lustre, and a specific gravity of 6.24. It burns in the air with a bluish flame, giving white fumes of tellurium dioxide.

197. Compounds. — 1. *Hydrogen telluride*, H_2Te, is a very poisonous gas resembling hydrogen sulphide. It is prepared thus: —

$$ZnTe + 2\,HCl = ZnCl_2 + H_2Te.$$

It burns with a blue flame, is soluble in water, and forms the tellurides.

2. *Tellurium dioxide*, TeO_2, is obtained by burning the metal in the air or in oxygen. It also occurs native in tellurite. When melted it forms a light-yellow liquid.

3. *Tellurous acid*, H_2TeO_3, is formed by dissolving the metal in dilute nitric acid and pouring the liquid into water.

4. *Tellurium trioxide*, TeO_3, is prepared by strongly heating telluric acid, thus: —

$$H_2TeO_4 = H_2O + TeO_3.$$

This oxide is an orange-yellow crystalline solid.

5. *Telluric acid*, H_2TeO_4, is produced by oxidizing tellurium with potassium nitrate.

198. Tests for Tellurium and its Compounds. — 1. Free tellurium, when dissolved in strong sulphuric acid, forms a purplish-red solution, from which tellurium may be precipitated by adding water.

2. Tellurium in any compound may be detected by mixing with sodium carbonate and a little charcoal dust, after which it is placed in a sealed tube and heated to redness. When cool the tube is broken and the contents dissolved in hot water. Sodium telluride, Na_2Te, is dissolved out, coloring the water purple. Upon standing, free tellurium is deposited.

3. Tellurates are first heated to redness, whereby they are reduced to tellurites. The tellurites when dissolved in hydrochloric acid and afterwards treated with sulphurous acid yield tellurium.

EXERCISES.

1. In what experiment did sulphur *unite directly with a metal* to form a sulphide? In how many ways may a salt be formed?

2. What varieties of sulphur may be purchased at the drug store? (SUG. Ask your druggist what varieties he has for sale, and by what names they are known.)

3. Try to obtain sulphur from a piece of vulcanized rubber.

4. Try to prepare H_2S from various sulphides that you may find in the laboratory. Use H_2SO_4, HCl, and HNO_3. Try "Fool's Gold" or iron pyrites. If the acids do not give the desired results, fuse the pyrites on charcoal with sodium carbonate and again apply the acids. Do you thus obtain H_2S? Why?

5. The *amount* of hydrogen sulphide in a solution, as in mineral water, may easily be determined by titration. For this purpose a standard solution of iodine and a fresh solution of starch paste (an indicator) are required. The standard solution is prepared thus:—

Weigh out in a small corked vial (weighing flask) about 1^g of pure iodine; then dissolve about 5^g potassium iodide in 20^{cc} distilled water; uncork the vial and immerse it in the iodide solution. When the iodine is dissolved, dilute with water so that 1^{cc} of the standard solution shall contain 1^{mg} of free iodine; preserve this in a perfectly corked bottle in a dark place.

The titration is made thus: To 100^{cc} of the water to be tested add about 2^{cc} starch paste, and then, in the usual manner, add the standard solution of iodine, until a permanent light-blue color is reached. The number of cubic centimetres standard solution required (N) equals the number of milligrams of iodine required to decompose the hydrogen sulphide:—

$$2\,I + H_2S = 2\,HI + S.$$

It is usually safe to deduct from N 1 or 2^{mgs} to allow for the iodine required to color the starch paste, although this is best determined by trial. (As soon as the H_2S is decomposed, upon what does the I act? What causes the blue color?)

The computation is made thus:—

$$254 : N :: 34 : x = \text{wt. of } H_2S \text{ in } 100^{cc}.$$

In case the amount of H_2S per litre is required, it = 10 x. Why? How obtain the number of cubic centimetres of H_2S gas per litre? Whence come the numbers, 254 and 34? How compute the number of cubic inches of H_2S per U.S. gallon?

6. Coal containing much sulphides is not adapted to reducing iron from its ores. Why? Sometimes the sulphides are oxidized to sulphates, which are not so objectionable, by piling coal in heaps exposed to the air:—

$$FeS_2 + xO = \;.\;.\;.\;?$$

7. Try to obtain a sulphate by treating sulphur or a sulphide with a mixture of $KClO_3$ and HNO_3. Test for the sulphate with $BaCl_2$.

8. Sulphuric acid or a sulphate is determined *quantitatively*, thus: To (say) 50^{cc} of the solution containing a sulphate (*e.g.*, K_2SO_4) add hydrochloric acid and boil; while hot add an excess of barium chloride and thoroughly agitate:—

$$BaCl_2 + K_2SO_4 = BaSO_4 + 2\,KCl.$$

Now filter out the $BaSO_4$ and thoroughly wash with much hot water; the ash of the filter-paper used should be known; the precipitate and filter-paper are now carefully dried and the precipitate carefully transferred (as completely as possible) to a weighed porcelain crucible; the filter-paper is now burned and its ash placed within the crucible, which is then heated to redness; when the crucible is cool its weight (W) is determined:—

$$W - \text{wt. of cruc.} - \text{wt. of filter-ash} = \text{wt. of } BaSO_4.$$

Sometimes the chemist estimates the anhydride of an oxacid. How much SO_3 in 17.241^{g} $BaSO_4$? With how much potassa, K_2O, will this amount of SO_3 unite, and how much K_2SO_4 will it yield?

9. The salts of many acids are decomposed and their acids set free by sulphuric acid. Why?

Complete and balance these equations:—

$$\begin{aligned} &KNO_3 + H_2SO_4 = \ldots \\ &NaCl + H_2SO_4 = \ldots \\ &Na_2CO_3 + H_2SO_4 = \ldots \end{aligned}$$

10. Make a table showing the similarity of the formulae of the oxides and acids of S, Se, and Te.

11. AN EXERCISE IN VALENCE. If to the number representing the valence of an element we assign a positive or negative sign, we shall find that the algebraic sum of these numbers in any stable chemical compound always equals zero,—provided we take:—

1. The number for $H = +1$.
2. The number for $O = -2$.
3. The number for any metal in combination as + (except As, Sb, etc., with H).

We may utilize these data *to determine the valence* of an element in combination; *e.g.*, what is the valence of I in HIO_3?

SOLUTION. $O_3 = 3 \times -2 = -6$. $H = +1$. Now the question simply is, what number must be added to the $+1$ to make $+6$ (or a number which added to -6 will give 0). The number required is evidently $+5$. Accordingly we may conclude that I in HIO_3 is a *pentad*.

QUERIES. What is the valence of S in the following compounds: H_2S; H_2SO_2; H_2SO_3; H_2SO_4; $H_2S_2O_3$? Of Cl in: HCl; HClO; $HClO_2$; $HClO_3$; $KClO_4$? Of Br in: HBr; HBrO; $HBrO_3$; $HBrO_4$? Of P, Si, B, and N in their compounds?

SUG. Read *Johnson on Oxidation* in Douglas and Prescott's *Qualitative Analysis*, pp. 251–253.

CHAPTER XII.

SILICON AND BORON.

SILICON.

SYMBOL, Si^{iv}. — ATOMIC WEIGHT, 28. — SPECIFIC GRAVITY, 2.49.

199. Occurrence. — Silicon is a very abundant element, occurring in combination with oxygen, or with oxygen and other elements. Silica, SiO_2, known under the names quartz, sand, agate, etc., is a very widely distributed substance, found in every geological formation.

The silicates, such as feldspar, mica, and certain clays, are well-known compounds. Silicon constitutes from 22.8 to 36.2 per cent of the earth's crust.

In a free state, it may be prepared in three modifications, — amorphous, graphitoidal, and crystalline.

200. Preparation. — EXP. 123 T. Silicon may be obtained by heating in an iron tube potassium hydrofluosilicate, K_2SiF_6, with metallic sodium or potassium: —

$$K_2SiF_6 + 4\,K = 6\,KF + Si.$$

A violent reaction occurs. When cool the fused mass is treated with water to dissolve the potassium fluoride, while the silicon remains as a brown *amorphous* powder. (See Art. 208 for K_2SiF_6.)

EXP. 124 T. Place in a porcelain crucible a small quantity of amorphous silicon. Carefully lute on the cover with a paste of wood ashes, and after thoroughly drying heat the crucible, gently at first, and finally to redness. The amorphous mass contracts, becoming denser, and assuming the form of *plates of graphite*.

Exp. 125 T. *Crystalline silicon* is best obtained by the following method: A mixture of 3 parts dry sodium hydrofluosilicate, Na_2SiF_6, and 1 part sodium cut in pieces, is rapidly introduced into a hessian crucible heated to bright redness. Then 9 parts well dried granulated zinc are rapidly added; and finally, the whole covered with a layer of dried sodium chloride. The crucible is then closed, the fire allowed to go down, and the crucible allowed to cool in the furnace. The silicon under these circumstances crystallizes from its solution in molten zinc, and the zinc afterward solidifies, enclosing the crystals of silicon. By treating the mass with hydrochloric acid the zinc is dissolved and the crystals left behind.

201. Properties.—Amorphous silicon, as obtained above, is inflammable in the air, when strongly heated, producing silicon dioxide. The graphitoidal form is not so readily inflammable. At a high temperature, and in absence of oxygen, silicon can be fused. Hydrochloric acid does not dissolve it, but in strong alkalies it is soluble, thus:—

$$Si + 2\,KOH + H_2O = K_2SiO_3 + 2\,H_2.$$

NOTE. The student will not meet with free silicon in his work unless he prepares it or buys it as such, when he can examine it, ignite it, and test for silicon dioxide. Art. 205.

SILICON AND OXYGEN.

SILICON DIOXIDE, OR SILICA, SiO_2.

202. Occurrence.—Silicon and oxygen form one well-known compound, which occurs in many modifications, as:

1. *Quartz crystals*, glassy hexagonal prisms terminating in hexagonal pyramids.
2. *Amethyst*, *smoky quartz*, *rose quartz*, and *chrysoprase*, colored varieties of quartz.
3. *Quartzite*, a sedimentary rock.
4. *Sand* and *sandstone*, fine fragments of quartz more or less cemented together.
5. *Honestone* or *novaculite*, a fine-grained quartz rock.
6. *Chalcedony*, a mixture of crystalline and non-crystalline quartz.
7. *Agate*, consisting of layers of crystallized and amorphous quartz of various colors.
8. *Flint* and *chert*, a coarse variety of chalcedony.
9. *Opal*, a hydrated form of silica.
10. Various modifications of the above in which one form is passing into another.

203. Preparation. — Silica may be artificially obtained in two forms: as the so-called "soluble silica," and as an insoluble powder.

Exp. 126 p. Melt in a crucible, 6^g each, potassium carbonate and sodium carbonate; then add 3^g pulverized quartz or white sand, and heat till the whole is melted. The molten mass is now to be poured out and dissolved in dilute hydrochloric acid. The solution thus obtained is now placed in a tray (dialyzing), which may be prepared by stretching parchment paper over a wooden hoop, say 10^{cm} in diameter. This tray is now floated on a tub of pure water, when the hydrochloric acid and saline substances of the solution pass through the parchment into the water of the tub, while the soluble silica remains in the tray. It will take about four days to effect this separation, and there must be much water in the vessel on which the tray is floated, or it must be often changed.

Note. This method of separation is called *Dialysis*, and depends upon the fact that crystallizable substances will pass through the parchment, while colloid or non-crystallizable substances will not pass through.

In this manner a colorless, tasteless, limpid solution is obtained, which may be concentrated in a generating-flask; but if the concentration be carried too far, the solution becomes of a jelly-like consistency.

Though we here speak of having silica in solution, the substance dissolved is really a form of silicic acid, probably ortho-silicic acid, H_4SiO_4. This loses water very readily, and is converted into meta-silicic acid, H_2SiO_3, and this, when dried, loses more water, and passes into silicon dioxide, SiO_2.

Note. The relations between silicon dioxide and silicic acid, H_2SiO_3, are similar to those existing between carbon dioxide and carbonic acid. Student will indicate the points of resemblance.

Exp. 127 p. Evaporate strictly to dryness (in an evaporating-dish) a portion of the solution obtained in the last experiment. The powder thus obtained is pure silica. Is it now soluble in acids? In alkalies?

204. Properties. — Natural crystals of silicon dioxide or quartz are of a glassy lustre, and rank 7° in the scale of hardness. They present no cleavage, and a conchoidal fracture. The specific gravity of quartz is 2.6; of tridymite, another form, it is 2.3.

All forms of silica are somewhat soluble in alkalies, especially when digested under pressure; consequently many waters, such as those of the Hot Springs in Arkansas, and the geysers of Iceland, contain, in solution, silica, which is deposited upon standing. This explains the existence of siliceous sedimentary rocks, like quartzite, etc., and of the siliceous petrifactions which so frequently occur, especially in the rocks of the Cretaceous Period.

Tripoli is the siliceous remains of the shells or valves of microscopic plants, — the Diatoms.

Sandstone is composed of fragments of quartz cemented together by deposited silica; while

Conglomerates are larger pebbles similarly joined. Artificial conglomerate is now used as a building stone.

The many different colors which quartz assumes are due to the fact that soluble silicon compounds readily absorb coloring matters. These colors are either destroyed or changed upon application of heat.

Some forms of quartz, owing to their hardness, and susceptibility to a high polish, are prized as ornaments.

Agates are somewhat porous; when soaked in honey, then treated with sulphuric acid, and afterwards polished, they exhibit curious and beautiful markings.

205. Tests for Silicon Dioxide. — The student will soon learn to recognize any of the natural forms of silica by their appearance when crystallized, and by their hardness and fracture. (Also see tests for Silicates.)

THE SILICON OXACIDS.

206. The silicon acids are hardly known in the free state, being very unstable like carbonic acid. Notwithstanding the instability of the acids of this series, there are three well-marked classes of salts which we may fairly suppose to be derived from these acids: —

1. The mono-silicates.
2. The bi-silicates.
3. The tri-silicates.

Wollastonite, $CaSiO_3$, and steatite, $Mg_3H_2(SiO_3)_4$, are examples of the first; serpentine, $Mg_3Si_2O_7$, and orthoclase, $Al_2K_2(Si_3O_8)_2$, are examples of the second and third. Besides these there are known many polymeric forms of each of these classes.

SUG. Read R. and S., Vol. I., p. 573.

The various forms of silicic acid may be regarded as derived from the acid H_4SiO_4 by abstraction of water in different proportions. The simplest case is represented thus: —

$$H_4SiO_4 - H_2O = H_2SiO_3,$$

the salts of the acid thus formed being the monosilicates. Then we have: —

$$2\,H_4SiO_4 - H_2O = H_6Si_2O_7,$$

from which the bisilicates are derived; and, finally,

$$3\,H_4SiO_4 - 4\,H_2O = H_4Si_3O_8,$$

from which the trisilicates are derived.

207. Tests for the Silicates. — Fuse the solid substance with sodium carbonate on charcoal; dissolve the fused mass in hydrochloric acid, and evaporate the solution to dryness. If a white powder (SiO_2), insoluble in hydrochloric acid, and soluble in potassium hydroxide, be obtained, silicic acid, or some of its derived forms, is present.

OTHER COMPOUNDS OF SILICON.

208. Silicon may be made to unite with nearly all the elements previously considered, but their compounds are unimportant. We may mention here that; —

1. *Silicon hydride*, SiH_4, is a gas prepared by acting upon an alloy of magnesium and silicon with very dilute hydrochloric acid, in the absence of air.

If this gas be allowed to escape through water in bubbles, each bubble, upon coming in contact with the oxygen of the air, ignites spontaneously, forming ring-shaped clouds of silicon dioxide.

2. *Silicon fluoride*, as we have previously seen, is obtained by acting upon glass or silicon with hydrofluoric acid (Art. 134).

3. *Hydrofluosilicic acid*, H_2SiF_6, is prepared when silicon fluoride is dissolved in water: —

$$3\,SiF_4 + 4\,H_2O = H_4SiO_4 + 2\,H_2SiF_6.$$

The sodium or potassium salts of this acid may thus be prepared: —

EXP. 128 T. Silicon fluoride is first prepared by treating in a generating-flask sand and fluorspar, CaF_2, with sulphuric acid. This gas is led into water, thus forming a solution of hydrofluosilicic acid. When potassium or sodium carbonate is added to this solution, a precipitate of the sodium or potassium salt is obtained. Care must be taken to avoid an excess of the alkaline carbonate, as the salts of hydrofluosilicic acid are decomposed by alkalies.

BORON.

SYMBOL, B'''. — ATOMIC WEIGHT, 11. — SPECIFIC GRAVITY (CRYSTALS), 2.5.

209. Occurrence. — Boron occurs only in combination with other elements. The chief compounds are boric acid, H_3BO_3; borax, $Na_2B_4O_7 + 10\,H_2O$; and boracite, $2\,Mg_3B_8O_{15}, MgCl_2$.

210. Preparation. — Boron may be prepared in two modifications, viz., amorphous and crystalline.

Exp. 129 T. Amorphous boron, a dark-brown, odorless, tasteless powder, may be obtained by heating boron trioxide, B_2O_3, with metallic potassium in an iron tube.

Exp. 130 T. Crystalline or adamantine boron is obtained by fusing amorphous boron, in the absence of air, with metallic aluminium.

This modification of boron ranks 9° in the scale of hardness, and its crystals are prisms or monoclinic octahedra.

211. Boron Compounds. — 1. *Boron trioxide*, B_2O_3, is the only known oxide of boron, and may be obtained by heating to redness boric acid, H_3BO_3. It is a brittle, glassy solid, readily uniting with water to form boric acid.

Sug. Write the equation.

2. *Boric acid*, H_3BO_3, occurs dissolved in the waters of certain lagoons in Tuscany, and the market is mostly supplied from that source. In the vicinity of these lagoons are volcanic jets of steam, whose heat is used to evaporate the water containing the acid, which is thus obtained in crystals; its purification is effected by recrystallization from a water solution.

There are in California several dried up lake beds containing massive borax, said to be sufficient to supply our wants. Here the acid is obtained by treating the borax with hydrochloric acid, and dissolving in hot water. From this solution boric acid is also obtained by crystallization.

Boric acid is soluble in water and in alcohol. It forms the *borates.*

212. Tests for Boric Acid and the Borates.—1. When in solution, the free acid turns a strip of turmeric paper brown, and this color is not changed by dilute hydrochloric acid, as is the case with the alkalies.

NOTE. It is best for the beginner to compare the action of an alkali on this paper with the action of boric acid, noting how the hydrochloric acid affects the colors. Also dip a piece of turmeric paper in boric acid; then moisten with Na_2CO_3 and note the greenish-black color produced.

2. When a solid borate is heated on a platinum loop in the reducing flame, the flame is tinged green.

NOTE. This test is most striking when the solid has first been calcined, then dipped in sulphuric acid and heated to expel the acid, and finally moistened with glycerine and treated as in 2.

EXERCISES.

1. Silicates in solution are estimated quantitatively as follows: The solution is acidulated with hydrochloric acid and evaporated strictly to dryness, without allowing the temperature to rise sufficiently high to cause the silica, SiO_2, obtained again to unite with any bases present. The residue is again treated with hydrochloric acid; the white insoluble powder SiO_2 is next removed by filtration, and in a manner similar to that employed in estimating the sulphates directly determined as silica.

2. Soak bits of agate in honey; treat with sulphuric acid, and polish on a grindstone or emery wheel. The peculiar markings of the agates are thus brought out.

3. Unite the edges of broken bits of glass with the so-called "soluble silica"; allow the mended articles to dry for two days; then test the strength of the silica as a cement.

4. What is glass? Write an essay on the manufacture of glass.

5. Ask a blacksmith for what purposes he uses borax. Ask him if a mixture of salt and sand will answer as well. What is a flux?

6. For what use does the barber employ borax?

7. Does borax soften "hard" water? Try it.

8. What is the anhydride of boric acid, H_3BO_3?

9. Dissolve a little borax in HCl; then to the solution add alcohol. Warm and ignite the alcoholic solution of boric acid thus obtained and note the characteristic *green* flame.

10. The waters of all our streams abound in diatoms. Examine some under the microscope.

CHAPTER XIII.

PHOSPHORUS. — ITS OCCURRENCE, COMPOUNDS, ETC. — GENERAL EXAMINATION OF UNKNOWN SUBSTANCES FOR ACIDS.

PHOSPHORUS.

SYMBOL, P. — ATOMIC WEIGHT, 31. — SPECIFIC GRAVITY, 1.83.

213. Occurrence. — Owing to its great affinity for oxygen, phosphorus, although widely distributed, never occurs in the free state. Its principal compounds are with calcium; as, phosphorite, $Ca_3(PO_4)_2$, and apatite, $3\ Ca_3(PO_4)_2 + CaClF$. It also unites with iron to form vivianite, $Fe_3(PO_4)_2 + 8\ H_2O$. It is also found in the igneous rocks, from whose disintegration our alluvial soils have been produced; hence every fertile soil must contain phosphates. These phosphates are taken up from the soil by growing plants, of whose ripened seeds they form an essential constituent. Again, animals consume the plant and its seeds, and appropriate the phosphates for building up the solid or inorganic portion of their bones; and it is from bones that the greater part of our commercial phosphorus is now obtained. Sombrerite, an impure form of calcium phosphate, found in the island of Sombrero, is another source of commercial phosphorus.

214. Preparation. — Phosphorus is obtained from the ashes of burned bones. As a matter of economy, the bones are not directly burned, but are subjected to a preliminary treatment, in order to save some of their other constituents. Thus they are either first digested with water, under pressure, in closed vessels, in order to extract the gelatine; or they are distilled in closed retorts, the volatile products (bone oil) being utilized to some extent; while the remaining solid substance, or "bone black" is used for clarifying sugar until worthless for that purpose. In either case the remaining solid residue of the bones is reduced to ashes by burning in the open air.

Bone ash, which consists largely of calcium phosphate, $Ca_3(PO_4)_2$, is first treated with sulphuric acid, when an acid calcium phosphate, soluble in water, is obtained: —

$$Ca_3(PO_4)_2 + 2\,H_2SO_4 = \underline{CaH_4(PO_4)_2} + 2\,CaSO_4.$$

This solution of "super-phosphate of lime," as it is usually called, is then evaporated to dryness, and afterward heated nearly to redness, when calcium meta-phosphate is obtained: —

$$CaH_4(PO_4)_2 = \underline{Ca(PO_3)_2} + 2\,H_2O.$$

The meta-phosphate is then intimately mixed with fine charcoal dust, and heated to redness in earthen crucibles placed in tiers inside of a furnace, their necks extending outside of the furnace, and dipping under water in a condenser. Only one-half of the phosphorus is thus liberated and condensed under the water. The phosphorus is now removed, melted under water, and purified by straining through chamois leather under water, when it is cast into the ordinary sticks of commerce. Before it is cast into sticks, the phosphorus may be purified by treating it with sulphuric acid and potassium dichromate, $K_2Cr_2O_7$.

All the phosphorus contained by the bone ash may be liberated by mixing the meta-phosphate with sand and charcoal dust, after which it is treated as before. The reactions are:—

1. $2\,Ca(PO_3)_2 + 5\,C = Ca_2P_2O_7 + 5\,CO + 2\,P.$
2. $2\,Ca(PO_3)_2 + 2\,SiO_2 + 10\,C = 2\,CaSiO_3 + 10\,CO + 4\,P.$

215. Properties.—Phosphorus is a highly inflammable substance, taking fire at low temperatures. When exposed to the air it slowly oxidizes, emitting a phosphorescent glow, or luminous and evanescent flashes of light. A slight blow or scratch is often sufficient to ignite it. It burns with great heat, and when in contact with the flesh it produces deep and painful wounds; hence great care should be exercised in handling it. It should not be taken in the hands nor cut in the air, but should be held by a pair of forceps, and cut under water.

Phosphorus should always be stored, for safe keeping, in a bottle of water fitted with a good cork to prevent the water from evaporating; the bottle should then be kept in a tightly-covered can, and the whole placed in a cool place.

Owing to the low temperature of its ignition, phosphorus is employed in tipping the common lucifer match. The composition of match-tips varies; but nearly all the compounds employed for making tips contain phosphorus, sulphur, and potassium nitrate.

Phosphorus is also used as an ingredient of many vermin "exterminators," but about five-sixths of all the phosphorus produced is consumed for making matches.

The fumes of phosphorus are characteristic, possessing poisonous properties, and an odor with a faint resemblance to garlic. When taken internally, phosphorus is a virulent poison; one decigram may produce fatal results. Severe pains in the stomach, vomiting of substances with an odor of garlic, and even the characteristic fumes emitted with the breath, are the symptoms of phosphorus poisoning. Turpentine is a proposed antidote.

Phosphorus is known in three different modifications, viz.: —

1. *Ordinary*, or *waxy phosphorus*, the form usually seen in sticks.

2. *Crystalline phosphorus*, obtained by dissolving the common form in carbon bisulphide, and allowing the solution to evaporate.

3. *Red*, or *amorphous phosphorus*, obtained when either of the other two modifications is heated to 240° in the absence of the air. This variety is not so inflammable as the ordinary phosphorus, nor does it give off poisonous fumes; hence it is sometimes used by the matchmakers, who thus avoid the dreaded effects of phosphorus poisoning. The specific gravity of this variety is 2.106.

All three varieties of phosphorus burn in the air with a bright, luminous flame, forming dense white fumes of phosphorus pentoxide.

QUERY. Should an excess of phosphorus be employed in experiment 41, of what variety would the remainder be?

216. Tests for Free Phosphorus.—1. Phosphorus, in considerable quantity, may be detected by its physical properties and odor.

2. In minute quantity, as in cases of phosphorus poisoning, phosphorus is detected by dissolving in water the substance to be tested, after which it is boiled in a generating-flask, and the steam is led through a glass condensing-tube into another flask containing cold water.

Now, if the room be dark, and if phosphorus be present, a phosphorescent glow is noticeable at the point where the steam condenses.

PHOSPHORUS AND HYDROGEN.

217. Phosphorus and hydrogen form three compounds:—

1. Gaseous phosphoretted-hydrogen or hydrogen-phosphide, PH_3.
2. Liquid phosphoretted-hydrogen or hydrogen-phosphide, PH_2.
3. Solid phosphoretted-hydrogen or hydrogen-phosphide, (P_2H?).

Of these we shall consider only the first.

218. Gaseous Hydrogen Phosphide, or Phosphine, PH_3, is a gas which ignites spontaneously upon coming in contact with the oxygen of the air, owing to the presence of traces of the liquid compound PH_2, this latter substance being obtained by the same process that yields the former. If the tube from which the phosphine escapes be bent upward under water, each bubble upon reaching the air ignites, forming beautiful ring-shaped clouds of phosphorus pentoxide, P_2O_5. In a still atmosphere these clouds have a peculiar rotary motion, illustrating what is known as *vortex motion.* This striking experiment may be exhibited thus:—

Exp. 131 T. In a generating-flask place a strong solution of potassium hydroxide, KOH, and add several small pieces of stick phosphorus. Now gently warm, and as soon as flames begin to appear at the mouth of the flask, insert a cork carrying a bent delivery-tube. The lower end of this tube is to dip under water placed in an open vessel. As each bubble of the gas comes into the air, it ignites with a slight report:—

$$4P + 3KOH + 3H_2O = 3KH_2PO_2 + PH_3.$$

It is somewhat safer to put the apparatus together, and then to pass hydrogen through it long enough completely to displace the air; or the air may be expelled by pouring a little ether over the solution before warming. During the experiment currents of air in the room are to be avoided. Save the contents of the generating-flask for work under hypophosphorous acid.

QUERIES. What is the object of these last precautions? What other gas behaves like PH_3? Show how PH_4Br and PH_4I are obtained from PH_3, HI, and HBr. Does PH_3 form salts similar to NH_3?

In this experiment liquid hydrogen-phosphide may be obtained by passing the gas through a suitable condensing-tube, but both this and the solid form are of no importance to the beginner. None of the hydrogen phosphides possess acid properties.

SUG. Make a list of the binary acids. Also make a list of the non-acid hydrogen compounds of the elements previously considered. Which one is alkaline?

PHOSPHORUS AND OXYGEN.

219. There are two known oxides of phosphorus, viz.: —

1. Phosphorus Trioxide, P_2O_3.
2. Phosphorus Pentoxide, P_2O_5.

1. *Phosphorus trioxide* is formed when phosphorus is burned in a limited supply of air. It is a white powder, which possesses a garlic odor, and unites with water to form phosphorous acid: —

$$3\,H_2O + P_2O_3 = 2\,H_3PO_3.$$

2. *Phosphorus pentoxide* is obtained by burning phosphorus in the open air or in oxygen. It is also a white powder, which eagerly unites with hot water to form phosphoric acid: —

$$3\,H_2O + P_2O_5 = 2\,H_3PO_4.$$

THE PHOSPHORUS OXACIDS.

220. There are three acids in this series: —

1. Hypophosphorous acid . H_3PO_2,
2. Phosphorous acid . . . H_3PO_3,
3. Phosphoric acid . . . H_3PO_4,

from which are derived: —

a. Metaphosphoric acid . . HPO_3,
b. Pyrophosphoric acid . . $H_4P_2O_7$.

Since the last two acids may be derived from phosphoric acid, all three will be treated under one article, after the consideration of the first two acids in the series.

HYPOPHOSPHOROUS ACID, H_3PO_2.

221. EXP. 132 P. In a generating-flask place 10^{cc} of a solution of barium hydroxide, $Ba(OH)_2$, and add two or three small pieces of phosphorus. Add a little ether and boil until the following reaction is completed: —

$$3\,Ba(OH)_2 + 2\,P_4 + 6\,H_2O = 3\,Ba(H_2PO_2)_2 + 2\,PH_3.$$

The remaining solution is now to be filtered, when the barium hypophosphite is obtained in clear solution. To this solution carefully add dilute sulphuric acid to precipitate the barium, when hypophosphorous acid is obtained, thus: —

$$Ba(H_2PO_2)_2 + H_2SO_4 = BaSO_4 + 2\,H_3PO_2.$$

This acid is a colorless liquid, oxidizing to phosphorous and phosphoric acids, when standing exposed to the air. It is *mono-basic*, only one atom of its hydrogen being displaceable. If we represent by M' any univalent metal, the general formula for a hypophosphite may be represented thus: $M'(H_2PO_2)$.

The hypophosphites may be prepared as in Exp. 131 T, by boiling phosphorus with an alkali. The principal use of these salts is for medicinal purposes. The acid and its salts are strong reducing agents.

222. Tests for Hypophosphorous Acid and the Hypophosphites. — 1. The acid or its salts when heated in a test-tube yield phosphine, PH_3.

$$2\,H_3PO_2 = PH_3 + H_3PO_4.$$

2. With silver nitrate a solution of the acid or its salts gives a white precipitate, which soon changes to brownish-black: —

$$4\,AgNO_3 + H_3PO_2 + 2\,H_2O = 4\,HNO_3 + H_3PO_4 + 4\,Ag.$$

3. To the solution of this acid or of its salts add an excess of cupric sulphate, $CuSO_4$; an insoluble hydride of copper, CuH, is formed. Boil a short time; hydrogen is liberated and metallic copper is obtained.

NOTE. No. 3 distinguishes H_3PO_2 from H_3PO_3. Thus test the latter.

SUG. Try hypophosphorous acid, or a hypophosphite, with mercuric chloride, $HgCl_2$. Do you obtain metallic mercury? In which tests do you find examples of reduction? Write the equations for $HgCl_2$ and $CuSO_4$ with KH_2PO_2.

PHOSPHOROUS ACID, H_3PO_3.

223. This acid may be obtained by passing chlorine gas through a layer of melted phosphorus under water. Phosphorus trichloride, PCl_3, is at first formed, and immediately reacts upon the water, thus: —

$$PCl_3 + 3\,H_2O = H_3PO_3 + 3\,HCl.$$

The hydrochloric acid is expelled by heat. If the addition of the chlorine gas does not stop short of saturation, *i.e.*, before the phosphorus has all disappeared, phosphoric acid is produced. Indeed, it is difficult thus to obtain phosphorous acid free from traces of phosphoric acid.

Phosphorous acid is generally *dibasic*, and $M'_2(HPO_3)$ may be taken as a general formula for the phosphites, although there are some phosphites known in which the acid is tribasic, all the hydrogen being displaced.

224. Tests for Phosphorous Acid or a Phosphite. — 1. To the solution add a few drops of sulphuric acid, and then add potassium permanganate until a purplish tint is reached. This color fades slowly in a cold solution, but rapidly when heat is applied.

SUG. Thus try H_3PO_2. How does it behave? Also try H_3PO_3 with $CuSO_4$, as you tried H_3PO_2. What results?

2. To the solution add calcium hydroxide, $Ca(OH)_2$; a white precipitate is thrown down.

SUG. Thus try a hypophosphite. Do you obtain a precipitate?

QUERY. How can you distinguish between a phosphite and a hypophosphite?

PHOSPHORIC ACID, H_3PO_4.

225. This acid is also known as *orthophosphoric* acid, and its salts as the *orthophosphates*. It may be obtained thus: —

EXP. 133 P. In an evaporating-dish place a small quantity of red phosphorus, and add reagent nitric acid (sp. grav. 1.2); now heat gently, adding more nitric acid, until the phosphorus disappears and red fumes cease to come off. The evaporation is to be continued until the excess of nitric acid is expelled.

The acid thus obtained is a thick, syrupy mass, free from odor and readily soluble in water; when allowed to stand, rhombic, six-sided crystals are obtained.

Phosphoric acid is a tribasic acid, forming acid and normal salts, the phosphates. M'_3PO_4 is a general formula for the phosphates.

Phosphoric acid is used in medicine, and its salts are of common occurrence and much used as fertilizers. The phosphates are found in the blood and fluids of animals; they are excreted from the kidneys as acid phosphate of sodium and phosphates of calcium and magnesium. When urea in urine decomposes a double salt of ammonium and sodium, $NaNH_4HPO_4$, or *microcosmic salt* is formed. It was from this source that, in 1669, Brandt first prepared phosphorus.

METAPHOSPHORIC ACID, HPO_3.

This acid is formed when orthophosphoric acid is heated to 400°. It is the form in which phosphoric acid is commonly met with in the market (glacial phosphoric acid). Its formation is illustrated thus: —

$$H_3PO_4 - H_2O = HPO_3.$$

At ordinary temperatures, in solution in water, it is slowly changed to orthophosphoric acid; the change takes place rapidly in boiling water.

Salts of metaphosphoric acid are formed by igniting phosphates belonging to the class represented by the formula $M'H_2PO_4$ as, for example: —

$$KH_2PO_4 - H_2O = KPO_3.$$

QUERY. In what process already considered does a transformation from an orthophosphate to a metaphosphate take place?

PYROPHOSPHORIC ACID, $H_4P_2O_7$,

Is formed when orthophosphoric acid is heated at 200–300°, until a small specimen neutralized with ammonia gives a pure white precipitate with silver nitrate. The change is: —

$$2\,H_3PO_4 - H_2O = H_4P_2O_7.$$

Its salts are formed by igniting phosphates of the order M'_2HPO_4, thus:—

$$2\,K_2HPO_4 - H_2O = K_4P_2O_7.$$

QUERY. In what connection have pyrophosphates been mentioned in this book?

226. Tests for the Phosphates or their Corresponding Acids.—1. To the solution add a few drops of silver nitrate, $AgNO_3$.

(*a*) A *light-yellow* precipitate, soluble in ammonia, nitric acid, and acetic acid, $H(C_2H_3O_2)$, indicates phosphoric acid or its salts.

(*b*) A *white precipitate*, soluble in nitric acid (without effervescence) and in ammonia, indicates pyrophosphoric acid or its salts.

(*c*) A *gelatinous white* precipitate, soluble in nitric acid, indicates metaphosphoric acid or its salts.

2. We may also distinguish metaphosphoric acid or its salts by acidulating its solution with acetic acid and adding the white of an egg, which immediately coagulates.

SUG. Try H_3PO_4 and $H_4P_2O_7$ with the white of an egg. What results?

3. The most delicate test for orthophosphoric acid or its salts is made by adding to the acid or to one of its salts dissolved in nitric acid an excess of ammonium molybdate, $(NH_4)_2MoO_4$; upon heating, a yellow precipitate of ammonium phospho-molybdate is obtained. See App. for reagent ammonium molybdate.

NOTE. This test is sufficiently delicate to detect even very minute traces of phosphoric acid or of the phosphates.

4. An orthophosphate with ammonium chloride, ammonia and magnesium sulphate, gives a crystalline precipitate of magnesium-ammonium phosphate, $MgNH_4PO_4$.

SUG. Try the phosphorus oxacids with salts of lead, calcium, barium, and mercury. What results?

EXAMINATION OF UNKNOWN SUBSTANCES FOR ACIDS.

227. We have now learned something about the principal inorganic acids. As we have already seen, Art. 79, some elements are acid formers, others form bases; and we may now mention that there are still other elements — as, for example, chromium and manganese — that are indifferent, acting in certain compounds as acids, in other compounds as bases. The consideration of the acids of the indifferent elements will be deferred for a time.

It frequently occurs that the chemist, while working, comes upon substances entirely unknown to him; and among other things that he is called upon to determine are the acids, which form essential constituents of all salts. It is true that the substance may not be acid, but, as we have previously seen, *the salt of any acid yields the test for that acid.* Thus, KNO_3 gives the test for nitric acid, and NaCl the test for hydrochloric acid, etc. Now since there are many acids, it is neither best nor profitable to test at random for first one acid and then another; some methodical plan should be followed. One method of procedure is as follows: —

If the substance be in liquid form and neutral, evaporate it to dryness or nearly so, carefully avoiding a high heat, which might decompose certain unstable compounds and drive off their acids in vapors. If the substance under examination be a solid, no preliminary treatment is necessary. If the substance in solution be acid, it is either a free acid or an acid salt; in this case the solution must be directly tested. Thus two cases naturally arise.

I. Let us suppose that the substance is neutral and a solid, or, if a neutral solution, that we have evaporated it to dryness. Proceed thus: —

Place a small portion of the substance in a test-tube; add sulphuric acid; heat it gently, and note the results as follows: —

1. *If a rapid effervescence of an odorless, colorless gas occur*, the substance is probably a carbonate or an oxalate. Now turn to the test for Carbonates or Carbonic Acid, Art. 152, and try a fresh portion of the substance by all the tests there given.

In case it prove not to be a carbonate, it is, very likely, an Oxalate, a salt of the organic oxalic acid, $H_2C_2O_4$. This acid (in this connection) may be recognized by its giving with calcium chloride, $CaCl_2$, a white precipitate of calcium oxalate, CaC_2O_4, soluble in hydrochloric acid, but insoluble in acetic acid.

2. *Slower effervescence of a colorless gas possessing odor.*

(*a*) The odor of *rotten eggs* indicates a sulphide. Test by Art. 169.

(*b*) The odor of *burning matches;* try for H_2SO_3, Art. 179, or $H_2S_2O_3$, Art. 186.

(*c*) Odor of *peach blossoms;* try for HCy, Art. 155.

(*d*) Odor of *vinegar;* try for acetates, which are the salts of acetic acid, $HC_2H_3O_2$, thus: Dissolve the original substance in water, add ferric chloride, Fe_2Cl_6, and boil. A red solution of ferric acetate, $Fe_2(C_2H_3O_2)_6$, is formed; the color is destroyed by adding hydrochloric acid.

(*e*) *An irritating odor* indicates HCl, Art. 96; HNO_3, Art. 75; or HF, Art. 135.

3. If a gas *having a color and an irritating odor* be liberated, try for HI, Art. 127; HNO_3, Art. 72; HClO, Art. 104; or HBr, Art. 117.

4. If a *sudden explosion occur*, try for $HClO_3$, Art. 108.

5. If none of the preceding phenomena occur, try for H_2SO_4, Art. 183; H_3PO_4, Art. 226; H_3PO_3, Art. 224; H_4SiO_4, Art. 207; H_3BO_3, Art. 212; HIO_3, Art. 131; or $HBrO_3$, Art. 121.

The student should remember that the foregoing data are valuable as *indications* only, and that these indications point toward certain acids to which he should refer, and which he should try until he is satisfied that he has found the right one.

II. If the solution be an acid one, proceed thus: —

1. To a portion of the solution add HCl; then add $BaCl_2$. If a *white precipitate* be obtained, the acid present is H_2SO_4, since barium sulphate, $BaSO_4$, is the only barium salt (except the salt formed with the rare acid H_2SiF_6) which is insoluble in hydrochloric acid.

2. To a fresh portion of the solution add HNO_3, and then $AgNO_3$.

The following acids give a precipitate insoluble in nitric acid: HCl; HI; HBr; H_2S; HCy; HClO; and the rarer acids, hydro-ferro-cyanic acid, H_4FeCy_6, and hydro-ferri-cyanic acid, H_3FeCy_6. For these last two acids, see Iron.

3. Test in order for the following acids, using each time a fresh portion of the solution: HNO_3; H_2CO_3; H_3PO_4; H_4SiO_4; H_3BO_3; $H_2S_2O_3$; H_2SO_3; HNO_2; $H_2C_2O_4$; $H(C_2H_3O_2)$; $HClO_3$.

If the acid is not discovered by working carefully up to this point, it is a rare acid, and the student will be obliged to try for all those previously mentioned in the text and not mentioned above. It is true that the acid may be quite a common one, belonging to the acids of the indifferent acid-forming elements, such as chromium, arsenic, or manganese.

In such a case the student needs farther experience to determine the acid. He will find directions under the elements just named.

EXERCISES.

1. Phosphorus in iron ores, or in coal used in reducing iron ores, makes the iron brittle. The presence of phosphorus in coal may be determined by testing the ash for phosphates.

2. Make a list of the commonly occurring acids; also a list of the rarer acids previously mentioned. In testing for acids a substance that occurs native, would you expect to find rare acids?

3. Dissolve the salt of an acid, and test with litmus paper; some salts are acid, some are neutral, and some are alkaline. By trying many salts and tabulating the results, the student may learn that normal salts may belong to any of the three classes. Do any of the *acid* salts that you have tried belong to the last two classes?

4 If in an unknown solution NH_3 and HNO_3 be found, what salt is present? If Na and HCl, what salt?

5. The student should be assigned many unknown (to him) salts and, by reference to the text, he should determine the acids present. In this way he will soon *know* the tests for the common acids. More than one acid may be assigned in one solution, provided the acids do not decompose one another, or their tests do not interfere. The metals of many metallic salts obscure the test for the acids of the salts; in this case the metals must first be removed, as will hereafter be explained. Na, K, NH_4, Ca, Mg, Sr, and Ba do not thus interfere.

6. For an improved method of obtaining phosphorus, see *Chemical News*, Apr. 4, 1879, p. 147.

CHAPTER XIV.

THE METALS.

INTRODUCTION.

228. The elements have been divided arbitrarily into **Metals** and **Non-metals**, but the dividing line is nowhere distinctly drawn. Certain elements, such as arsenic, antimony, and bismuth, stand midway, in regard to their physical and chemical properties, between the two proposed classes, and may be fairly placed in either; consequently we may justly consider the elements as forming but one class with a regular gradation of properties. In view of these facts it is impossible to give a strict and valid definition of a metal; but, in general, we may say: —

Definition. — A metal is an element which possesses a peculiar lustre, known as a metallic lustre, especially when in a solid or coherent condition, and the higher oxides of which only, and then in very few instances, are acid-forming compounds.

Sug. All, or nearly all, of the oxides of the non-metals form acids. State a few exceptions.

Note. Opacity, high specific gravity, and great atomic weight are not exclusively characteristic of the metals.

229. Properties of the Metals. — Some of the metals are barely known to exist, while others have been known since the highest antiquity, and their properties have been thoroughly investigated.

Of the properties of metals we may note the following: —

(*a*) *Specific Gravity.* — As a rule the specific gravity of a metal is greater than unity; only three — sodium, potassium, and lithium — are less than 1.000. Osmium (sp. grav. 22.48) is the heaviest metal, while lithium (sp. grav. 0.59) is the lightest. (See Art. 25.)

Queries. With what are solids and liquids compared to determine their specific gravities? Gases? How is specific gravity determined?

(*b*) *Specific Heat.* — The specific heat of an element is equal to the number of thermal units required to raise one kilogram of that element through 1° C.

The specific heat of any metal is less than unity, and varies somewhat according to the temperature at which the observation is made. The following observations, which were made at 55°, will serve as an illustration: —

Cd	0.0567	Co	0.1070
Zn	0.0955	Ni	0.1080
Ag	0.0570	Au	0.0324
Mn	0.1220	Pt	0.0324

(*c*) *Atomic Heat.* — When the specific heat of any element is multiplied by its atomic weight, a nearly constant quantity (about 6.4) is obtained. This product, in the case of any element, is termed the atomic heat of that element. Take, for example, gold and zinc: —

0.0324 (sp. ht. of Au) × 196.5 (at. wt. of Au) = 6.4 — (at. ht. of Au).
0.0955 (sp. ht. of Zn) × 65.0 (at. wt. of Zn) = 6.4 — (at. ht. of Zn).

From an inspection of the results thus obtained was deduced Dulong and Petit's law, viz.: —

The specific heat of an element varies inversely as the atomic weight of that element.

This law is but *approximately* true, but so nearly true that it is the best method known for selecting the atomic weights of some of the rarer metals. The accepted atomic weights of indium, cerium, didymium, and lanthanum were thus selected. For example, the atomic weight of cerium as determined by analysis of its compounds was at first assumed to be about 92 or 94, and the formulae of its principal oxides were taken as CeO and Ce_3O_4. The specific heat of cerium, however, was found to be 0.04479; this would make the atomic heat about 4.2 instead of 6.4. Accordingly the atomic weight was increased in the ratio $\frac{3}{2}$, and the same oxides were assigned the formulae Ce_2O_3 and CeO_2. Both hypotheses agree equally well with the percentage composition of these oxides.

QUERIES. In what different ways are the atomic weights of elements determined? If Ce = 94, what per cent of O is found in CeO and Ce_3O_4? If Ce = 141, what per cent is found in Ce_2O_3 and CeO_2?

(*d*) *The Conductivity* of the metals for heat and electricity is greater than that of the non-metals or any of the compounds of either.

(*e*) *The Melting-points of the metals*, so far as determined, vary from − 39° to + 1090° C. Iron and cobalt fuse at a white heat, platinum and iridium require the intense heat of the oxy-hydrogen blow-pipe, while osmium has not been fused at all. The determined melting-points of a few metals are: —

Hg	− 40°	Tl	+ 294°
G	+ 30°	Cd	+ 315°
K	+ 62.5°	Pb	+ 334°
Na	+ 95.6°	Zn	+ 423°
Li	+ 180°	Sb	+ 425°
Sn	+ 235°	Ag	+ 1000°
Bi	+ 270°	Cu	+ 1090°

It is difficult to measure the temperature required to melt a metal whose fusing-point is higher than that of copper.

(*f*) *The Molecular Heat of the Salts.*—The molecular heat of a metallic salt usually equals the sum of the atomic heats of its constituent elements: *e.g.*, the atomic heat of potassium is 6.5, that of bromine is 6.7, while the molecular heat of potassium bromide equals 13.2 or 6.5 + 6.7. The observed molecular heat of a salt agrees very closely with the theoretical results thus obtained.

230. Alloys.—Metals mix in definite and in indefinite proportions to form alloys, which possess properties both like and unlike the properties of the metals composing these alloys. These compounds are of great utility. The following list gives the composition of some of the principal alloys:—

1. *Gold Coin* (U.S.), 90 parts gold, 1 part silver and 9 parts copper.
2. *Silver Coin* (U.S.), 90 parts silver, 10 parts copper.
3. *Brass,* varying proportions of copper and zinc.
4. *Britannia,* varying proportions of brass, tin, antimony, and bismuth.
5. *Pewter,* 4 parts tin, 1 part lead.
6. *Queen's Metal,* 9 parts tin and 1 each of antimony, bismuth, and lead.
7. *Solder,* lead and tin in varying proportions.
8. *Speculum Metal,* 1 part tin, 2 parts copper.
9. *Bell Metal,* 18 parts tin, 22 parts copper.
10. *Bronze,* tin, copper, and zinc in varying proportions.
    Bronze Coin, 95 parts copper, 4 parts tin, and 1 part zinc.
11. *Type Metal,* 1 part tin, 2 parts lead, and 1 part antimony.
12. *German Silver,* 5 parts copper, 2 parts nickel, and 2 parts zinc.
13. *Fusible Metal* (melting at 93.75°), 1 part each of tin and lead, and 2 of bismuth. This is called "Rose's Metal."
    Fusible Metal (melting at 65°), 8 parts lead, 5 parts bismuth, 4 parts tin, and 3 parts cadmium. This is "Wood's Alloy."

SUG. Name the uses of the alloys.

231. Amalgams.—Certain metals, such as silver, gold, zinc, tin, copper, etc., unite with mercury to form amalgams. Some of these amalgams are of great value in the arts: battery zincs are amalgamated to prevent local currents and the needless waste of the zincs; mirrors are made by coating glass with a silver amalgam; articles to be electroplated are first slightly amalgamated to prevent the plating from peeling; gold and silver are extracted from their ores by amalgamation; etc.

QUERY. What uses does the chemist make of sodium amalgam?

Amalgams are made in different ways: —

(*a*) By the direct union of the metal with mercury. (Exp. 23.)

(*b*) By adding metallic mercury to the solution of a metallic salt: —

EXP. 134 P. To a solution of silver nitrate in a test-tube add a drop of metallic mercury. Allow the tube to stand some time. The splendid crystals formed are silver amalgam. These crystals often assume an arborescent form, whence the name, *arbor Dianæ.*

(*c*) By placing a metal in a solution of a salt of mercury: —

EXP. 135 P. Into a solution of a salt of mercury successively place bits of different metals, such as copper, iron, and zinc. Also try a nickel coin or a two-cent piece. What ones are amalgamated? Is the coating permanent?

SUG. Mercurous nitrate, $Hg_2(NO_3)_2$, is a good salt to use for this purpose.

GENERAL CAUTION. Do not bring mercury in contact with valuable articles, consisting of such metals as gold, silver, etc. Why?

232. Classification of the Metals. — Various methods of classification have been proposed and followed, such as a classification according to those properties which are made use of in the analysis of substances. Prominent among these properties are the *solubilities of the metallic chlorides*, *sulphides*, *hydroxides*, *carbonates*, and *phosphates* in various reagents. This method of classification is well adapted to the analytical separation and recognition of the various metals, while it interferes in no way with their proper consideration in other respects. To effect this separation in practice various *group reagents* are employed, and *five groups* are obtained: —

A. THE FIRST GROUP METALS.

In the separation of this group *hydrochloric acid* is the reagent employed, and all the metals belonging to the group may be precipitated as *chlorides*. We mean by this that any soluble salt containing a first group metal as a base gives, upon the addition of hydrochloric acid to a solution of that salt, an insoluble chloride. This group contains three metals: —

Lead	**Pb**,
Silver	**Ag**,
Mercury . . .	**Hg** (in mercurous salts only).

NOTE. Mercury, as we have already mentioned, gives two series of salts, which will be described under Mercury. The mercurous salts alone are precipitated by hydrochloric acid. The mercuric salts belong to the second group. It is necessary to state here that lead is not completely precipitated by hydrochloric acid.

B. THE SECOND GROUP METALS.

The metals of this group are characterized by yielding with *hydrogen sulphide*, H_2S, metallic *sulphides* which are insoluble in dilute acids. It is customary in analytical operations first to acidulate the solution with hydrochloric acid, and then to pass the hydrogen sulphide through the solution in question. If any or all the metals of this group are present, the precipitate obtained consists entirely of the sulphides of those metals. This group embraces the common metals: —

Arsenic	**As,**
Antimony	**Sb,**
Tin	**Sn,**
Bismuth	**Bi,**
Copper	**Cu,**
Cadmium	**Cd,**
Mercury	**Hg** (in mercuric salts);

and the rarer metals: —

Gold	Au	Ruthenium	Ru	Osmium	Os
Platinum	Pt	Iridium	Ir	Tungsten	W
Palladium	Pd	Rhodium	Rh	Molybdenum	Mo

NOTE. The sulphides of the first group are also insoluble in dilute acids and might be obtained in this group; but in the course of analysis it is best first to remove with hydrochloric acid the first group metals.

C. THE THIRD GROUP METALS.

The metals of this group are those whose hydroxides and sulphides are soluble in dilute acids but insoluble in alkaline solutions. *Ammonia* and *ammonium sulphide*, $(NH_4)_2S$, are the third group precipitants, and it is customary first to add to the solution under consideration ammonium chloride before adding the group reagents. This group includes the common metals: —

Iron	**Fe,**
Chromium	**Cr,**
Aluminum	**Al,**
Nickel	**Ni,**
Cobalt	**Co,**
Manganese	**Mn,**
Zinc	**Zn;**

and the rarer metals: —

Beryllium	Be	Cerium	Ce	Titanium	Ti
Indium	In	Didymium	D	Zirconium	Zr
Gallium	Ga	Terbium	Tb	Uranium	Ur
Yttrium	Yt	Erbium	E	Tantallum	Ta
Lanthanum	La	Thorium	Th	Niobium	Nb
		Vanadium	V		

NOTE. Many metals of this group form no sulphides in the wet way NiS and CoS are very sparingly soluble in cold dilute HCl.

D. THE FOURTH GROUP METALS.

We cannot isolate this group by means of their sulphides, etc., since these salts are soluble in acid and alkaline solutions. The metals of this group are separated by means of their *carbonates* which are thrown down by *ammonium carbonate*, $(NH_4)_2CO_3$, in solutions made alkaline with ammonia. The metals belonging to this group are: —

Barium	**Ba,**
Strontium	**Sr,**
Calcium	**Ca,**
Magnesium	**Mg.**

NOTE. The carbonate of magnesium is somewhat soluble in ammonia, and completely so in the presence of ammonium chloride; hence in practice it is customary first to add ammonia, ammonium chloride, and then ammonium carbonate. The magnesium salts are thus retained in solution and afterwards precipitated as a phosphate.

E. THE FIFTH GROUP METALS.

These metals give no precipitates with common reagents, since their salts are all soluble. This group includes: —

Potassium	**K,**
Sodium	**Na,**
Ammonium (known only in salts; see Ammonia),	**NH_4**
Lithium	**Li;**

and the rarer metals: —

Rubidium	Rb,
Cæsium	Cs.

In A, B, C, D, and E are outlined the general principles which, with a few details to be explained further on, enable us to separate the metals into groups. These groups may again be taken up and each metal separated and identified. It is thus that we may analyze a solution containing any or all the metals. It might be well here to give a definition of "analysis" as applied in chemistry.

1. *Qualitative Analysis* is the separation and detection of the individual substances in a given compound.

2. *Quantitative Analysis* is the determination of the weight or amount of each substance present in a given compound.

QUERY. Which analysis must be made first? Why?

233. Salts of the Metals. — The metals may be said to react with all the acids previously mentioned to form salts. The relations existing between the acids and the salts are, as a rule, simple and easily understood. A metal replaces a certain number of hydrogen atoms depending on its valence, a univalent metal replacing one hydrogen atom, a bivalent metal, two, etc.

The simplest salts are those which are derived from monobasic acids and univalent metals; as,

Potassium nitrate . . .	KNO_3,
Sodium nitrite	$NaNO_2$,
Potassium chlorate . .	$KClO_3$,
Lithium perchlorate . .	$LiClO_4$, etc.,

in each of which one atom of the metal replaces one atom of hydrogen, forming a normal salt, or one that contains no more replaceable hydrogen.

In the case of bivalent metals and monobasic acids the relations are also simple enough, one atom of the metal replacing two atoms of hydrogen in two molecules of the acid; as, for example:—

Calcium hypochlorite	$Ca(ClO)_2$,
Barium nitrate	$Ba(NO_3)_2$,
Copper nitrate	$Cu(NO_3)_2$,
Magnesium chlorate	$Mg(ClO_3)_2$, etc.

A monobasic acid generally yields but one salt with any given metal. A few curious exceptions to this rule will be mentioned further on.

Taking now a bibasic acid, its two hydrogen atoms may be replaced, (1) By two univalent atoms of the same kind, as in

Potassium sulphate	K_2SO_4,
Sodium carbonate	Na_2CO_3, etc.

(2) By two univalent atoms of different kinds as in

Sodium potassium carbonate, $NaKCO_3$,
Sodium ammonium sulphate, $Na(NH_4)SO_4$, etc.

(3) By one bivalent metal, as in

Barium sulphate	$BaSO_4$,
Zinc carbonate	$ZnCO_3$,
Copper sulphate	$CuSO_4$, etc.,

or (4) Only one of the hydrogen atoms may be replaced, thus giving rise to the formation of a substance which is called an *acid salt*, as in

Mono-potassium carbonate, $KHCO_3$,
Mono-sodium sulphate . $NaHSO_4$, etc.

The matter becomes more complicated when we have tribasic and tetrabasic acids, and trivalent and quadrivalent metals to deal with; but still the student should carefully trace the relation between the most complex acids and their salts. Most acids are either monobasic or bibasic, and only a few of those which we commonly have to deal with are tribasic.

Sug. Let the student classify according to their basicity all the acids thus far considered.

We shall learn that most metals which we commonly have to deal with are either univalent, bivalent, or trivalent.

A normal salt frequently unites with a hydroxide to form a *basic salt*, *e.g.*, —

$$Pb(NO_3)_2 + Pb(OH)_2 = 2\,Pb\left\{\begin{matrix}OH\\NO_3\end{matrix}\right..$$

Again, water may thus act on a normal salt, *e.g.*, —

$$Bi(NO_3)_3 + 2\,H_2O = Bi\left\{\begin{matrix}(OH)_2\\NO_3\end{matrix}\right. + 2\,HNO_3.$$

Basic mercuric sulphate may be supposed to originate thus: —

$$HgSO_4 + 2\,HgO = Hg_3SO_6.$$

The structures of some basic salts are exceedingly complex.

Exercise. Taking as examples of univalent metals, potassium, sodium, and ammonium (NH_4); of bivalent metals, calcium, barium, and strontium; and of trivalent metals, aluminium and chromium, let the student write the formulae of the following named salts: barium hypochlorite, calcium nitrate, mono-potassium phosphate, tri-silver phosphate, tri-calcium phosphate, aluminium meta-phosphate, barium iodate, chromium sulphate, potassium aluminium sulphate, magnesium ammonium phosphate.

Sug. The teacher should add to this list, practicing the student until it is evident that the principles involved are thoroughly understood.

A NATURAL CLASSIFICATION OF THE ELEMENTS.

234. As previously explained, the elements may be roughly divided into metals and non-metals. There are other characteristics affording methods of classification, such as valence, in which the elements may be classed as monads, diads, triads, etc. Again, as we have seen, there are elements bearing a close resemblance to one another in their chemical compounds, properties, etc., such as chlorine, bromine, iodine, and fluorine; or sulphur, selenium, tellurium, etc. But a true understanding of natural relationships requires a careful study of *all* the available properties of the elements and their compounds, and cannot be based upon any one characteristic alone.

That property of the elements which can be expressed with the greatest certainty and definiteness is the *atomic weight.* The *specific gravity*, although varying within certain limits, may assist us to compare those elements which are solid at ordinary temperatures. Again, we may use the *atomic volume*, which is found by dividing the atomic weight of an element by its specific gravity; the number thus obtained shows how many cubic centimetres of an element are required to weigh as many grams as there are units in the atomic weight of that element.

The following table presents a number of facts in regard to the best known and most distinctly characterized elements including all those whose atomic weights are less than 88. The lists of compounds are made as full as the limits of the table allow, *no facts being suppressed in the interests of any theory.* The student of nature will feel best satisfied with that arrangement or classification which most fully expresses the natural harmonies. Many discrepancies are still to be expected through our lack of knowledge, or our imperfect appreciation of chemical facts.

	Atomic Weight.	Atomic Difference.	Specific Gravity.[1]	Atomic Volume.[1]	Highest Hydrogen Compound.	Highest Oxygen Compound.	Lowest Oxygen Compound.	REMARKS.
H	1.0				H_2	H_2O_2	H_2O	
Li	7.0	6.0	0.59	11.9		Li_2O_2(?)	Li_2O	
Be	9.1	2.1	2.07	4.4		BeO	BeO	There is some reason for assuming for Be the at. wt. of 13.65 with the oxide Be_2O_3. Compare *Ozone*, p. 31.
B	11.0	1.9	2.5	4.1		B_2O_3	B_2O_3	
C	12.0	1.0	3.5	3.4	CH_4	CO_2	CO	
N	14.0	2.0	Gas.		NH_3	N_2O_5	N_2O	
O	16.0	2.0	Gas.		OH_2	O_3	O_2	
F	19.1	3.1	?		FH			
Na	23.0	3.9	0.97	23.7	Na_4H_2	Na_2O_2	Na_2O	
Mg	23.9	0.9	1.74	13.8		MgO	MgO	
Al	27.3	6.4	2.60	10.6		Al_2O_3	Al_2O_3	
Si	28.0	0.7	2.39	10.7	SiH_4	SiO_2	SiO_2	
P	31.0	3.0	2.20	12.8	PH_3	P_2O_5	P_2O_3	P_2O is suspected to exist.
S	32.0	1.0	2.05	16.	SH_2	SO_3	SO_2	
Cl	35.4	3.4	Gas.	26.	ClH	ClO_2	Cl_2O	Perchloric acid, $HClO_4$, suggests a hypothetical anhydride, Cl_2O_7.
K	39.0	3.6	0.87	45.4	K_4H_2(?)	K_2O_2	K_2O	
Ca	39.9	0.9	1.58	25.3		CaO_2	CaO	
Sc	44.0	4.1	?	?				
Ti	48.0	4.0	4. ?	12.5?		TiO_2	Ti_2O_3(?)	
V	51.2	3.2	5.5	9.2		V_2O_5	V_2O	
Cr	52.4	1.2	6.8	7.65		CrO_3	CrO	
Mn	54.8	2.4	7.14	7.6		Mn_2O_7	MnO	
Fe	55.9	1.1	7.86	7.09	FeH_2	Fe_2O_3	FeO	
Ni	58.0	2.1	8.90	6.31		Ni_2O_3	NiO	
Co	59.0	1.0	8.5	6.82		Co_2O_3	CoO	
Cu	63.3	4.3	8.9	7.13	Cu_2H_2	CuO_2	Cu_4O	
Zn	64.9	1.7	7.2	9.37		ZnO	ZnO	
Ga	68.0	3.1	5.9	11.5		Ga_2O_3		
As	74.6		5.6	13.1	AsH_3	As_2O_5	As_2O	[SeO_3.
Se	79.0	4.4	4.8	16.5	SeH_2	SeO_2	SeO_2(?)	H_2SeO_4 suggests
Br	79.7	0.7	3.19	25.	BrH			Br_2O, Br_2O_5, and Br_2O_7 are hypothetical anhydrides.
Rb	85.2	5.5	1.52	56.3		Rb_2O	Rb_2O	
Sr	87.2	2.0	2.5	34.4		SrO_2	SrO	
Ag	107.7		10.6	10.2		Ag_2O_2	Ag_4O	
I	126.5		4.95	25.6	IH	I_2O_5	I_2O_5	HIO_4 suggests the hypothetical anhydride I_2O_7.
Te	128.0	1.5	6.25	20.4	TeH_2	TeO_3	TeO_2	

The following table is based on that of a Russian chemist named Mendelejeff, but modified in view of suggestions from L. Meyer, Huth, and Muir: —

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[1] From Huth's *Das periodische Gesetz der Atomgewichte*, Frankfurt a. Oder, 1884.

Note. Cut this chart on this line, and then roll so as to fasten on gummed edge.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
R_2O	RO	R_2O_3	RO_2 RH_4	R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	
H 1							
Li 7	Be 9	B 11	C 12	N 14	O 16	F 19	
Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5	
K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe, Ni, Co 56 58.6 59
Cu 63	Zn 65	Ga 69	— 72(?)	As 75	Se 79	Br 80	
Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100(?)	Rh, Ru, Pd 104 104.5 106
Ag 108	Cd 112	In 114	Sn 118	Sb 120	Te 128	I 127	
Cs 133	Ba 137	La 139	Ce 141	Di 144	— 149(?)	— 150(?)	— — —
—	—	—	—	Er 166	— 167(?)	— 169(?)	
— 170(?)	— 172(?)	Yb 173	— 178(?)	Ta 182	W 184	— 190(?)	Ir, Os, Pt 192.5 193 194
Au 176	Hg 200	Tl 204	Pb 207	Bi 209	—	—	
—	—	—	Th 232(?)	— 237(?)	U		

Note. Spread gum on this edge.

In this table the elements are arranged in eight vertical columns, representing eight groups; while successive series are presented in nearly horizontal lines. These are made to incline slightly, so that on rolling the table Na will immediately succeed F, K will succeed Cl, and so on in a spiral line. The first eight or twelve elements present very marked individuality of character; some of these are typical of natural groups which follow. Elements of most distinct basic character are found towards the left; non-metals predominate in the upper and middle parts of Groups V., VI., and VII.; while the lower part of the table is marked by the more indifferent elements. A double spiral will be traced beyond Si (beginning with P and V respectively) and distinguished by **heavy-face** and light-face type.

Many familiar relationships can now be traced out; thus, K, Rb, and Cs are more closely related to each other than they are to Li and Na; Ca, Sr, and Ba are very closely related in their properties, while Mg resembles these elements in some respects and Zn and Cd in others. Very many facts in regard to the properties and compounds of the several elements may be fixed in the mind by the law of association when studied with the aid of this table, while they could only be retained by a severe effort of memory, if viewed independently.

It will be noticed that the first series has but one member; group VIII. is represented in the even series only, beginning with the fourth; and the element of highest atomic weight yet discovered is in the twelfth series, group VI. It is necessary to transpose I and Te in the table, in view of their properties. The blanks represent the probable position and approximate atomic weights of elements not yet discovered or investigated. When Mendelejeff published his table (in 1869) he left two blanks which have since been filled by Sc and Ga; and the properties of these elements agree very closely with those expressly predicted from the analogies indicated in the table. The true position of some of the rarer metals (especially those of the cerium group) is still uncertain; these are here arranged as in Muir's *Principles of Chemistry*.

The harmony of nature here exhibited is most impressive. Is it possible that the so-called elements are really compounds? Did the various "elements" of the earth and sun once exist as hydrogen, when our solar system was a nebula?[1] And will modern chemists ever revive the famed problem of the alchemists, and seek to turn the base metals into gold? Far more precious than gold is the search for *truth;* and the more we learn of science, the broader becomes our conception of what we know in part, and the deeper should be our reverence for the infinite thought of the Creator.

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[1] See a paper by F. W. Clarke in *Popular Science Monthly* for Feb. 1876, p. 463.

QUERIES.

1. In column 2, p. 220, how many numbers differ from whole numbers by less than 0.1 ? If the numbers are calculated by comparing with O = 16, they approximate still more closely to whole numbers.

2. In column 3, what differences are greater than 3 ? Which are less than 2 ?

3. In column 4, where do the numbers increase ? Where do they diminish ? Note the same in column 5.

4. What monads are indicated by the compounds of column 6 ? What diads ? Triads ? Tetrads ?

5. Note the valence indicated by the oxides in the table, or by any other compounds that you may know.

6. Imagine it possible to begin with an atom of hydrogen, and to build up an atom of each of the elements by successive additions of matter; can you show that the specific gravity of the product would alternately increase and diminish ? What kind of variation is observed in the atomic volumes ? In valence ?

7. At what points of the series are elements of strongly marked non-metallic (or electro-negative) character brought into juxtaposition with those of strongly marked metallic or electro-positive character ? Is this transition marked by a relatively large or small increase of weight ?

CHAPTER XV.

THE FIRST GROUP METALS.

The metals of this group are, as previously explained, Lead, Silver, and Mercury. They are of great importance, and are utilized in manifold ways.

LEAD.

SYMBOL, PB''.—ATOMIC WEIGHT, 207.—SPECIFIC HEAT, 0.0315.
—MELTING-POINT, 334°.

235. Occurrence.—Native, or free, metallic lead occurs in very small quantities in certain lead-bearing ores and in volcanic tufa. The principal source of lead is its sulphide, Galena, PbS. This ore is distributed throughout nearly every geological period, but the largest deposits in the United States are in the Lower Silurian. Nearly every ore of lead is argentiferous, *i.e.*, silver-bearing; and it is not uncommon to find lead associated with other metals, as copper, tin, zinc, arsenic, antimony, molybdenum, tungsten, etc.

236. Preparation of Metallic Lead.—EXP. 136 P. In a test-tube containing a solution of lead acetate, $Pb(C_2H_3O_2)_2$, place a clean strip of metallic zinc. A dark deposit of lead soon forms on the zinc. Complete the equation

$$Pb(C_2H_3O_2)_2 + Zn = \dots$$

Collect this deposit of lead, place it on charcoal, and cover with sodium carbonate; now heat the mass before the blowpipe (reducing-flame), when a bead of metallic lead is easily obtained. Place this bead on an anvil and strike it a light blow with a hammer. Is it *easily malleable?* Cut the flattened bead with a knife, and scratch it with the finger-nail, carefully noting the hardness, lustre, tarnish, etc.

Exp. 137 p. Take any lead compound or lead ore, such as red lead, Pb_3O_4, or galena, PbS; place it on charcoal, and heat it before the reducing-flame. Do you again obtain a bead? Try this bead as before.

Exp. 138 p. Solder to each terminal of a Grove, Grenet, or Bunsen battery (2 cells) a narrow ribbon of platinum foil. Place the platinum strips about 1^{cm} apart in a beaker-glass containing a strong solution of lead acetate. Treat the deposit obtained as before. Is this deposit lead?

Query. What is Electrolysis?

Lead is easily reduced from its ores, in consequence of which it has been known since the highest antiquity. In the smelting works, where it is preparèd from its ores, three distinct processes are employed: —

1. *The air reduction process.* In this process the ore employed is the sulphide, PbS, which is simply roasted in a reverberatory furnace until one portion of the sulphide is changed to the sulphate, $PbSO_4$, and another to the oxide, PbO; the heat is then increased, when the unaltered sulphide reacts with the oxide and sulphate thus: —

$$(a)\quad 2\,PbO + PbS = 3\,Pb + SO_2.$$
$$(b)\quad PbSO_4 + PbS = 2\,Pb + 2\,SO_2.$$

2. *The carbon reduction process.* In this process the sulphide is mixed with peat, or other carbonaceous material, and reduced in a blast-furnace. The first and second processes are adapted to very pure ores only.

QUERY. In what experiment did you obtain lead by a combination of these two processes?

3. *The precipitation process* is adapted to the preparation of lead from impure ores. In this process the ore is melted with cast iron or iron slag. A portion of the lead is obtained pure, while the remainder, contaminated with other metals, is afterwards so treated that all are saved.

QUERIES. In how many *different* ways can you prepare metallic lead? Why is not the zinc process an economical one?

237. Properties, Uses, and Compounds of Lead. — Lead is a soft, heavy, malleable metal possessing a high lustre, which is best seen on a freshly-cut surface. On exposure to the air this surface soon oxidizes, thus: —

$$4\,Pb + O_2 = 2\,Pb_2O.$$

The oxide Pb_2O is a bluish-gray substance which soon forms a coating over the exposed surface, and prevents further oxidation.

EXP. 139 P. Draw the dull surface of a bit of lead over a clean white paper. Note that the surface of the lead becomes bright, and that a black streak is made on the paper.

Lead is insoluble in pure cold water free from air, but water is seldom or never pure; hence water flowing through, or standing in, leaden pipes or vessels is almost certain to contain lead salts in solution. Now, since lead and its salts affect the system as a virulent, cumulative poison, such waters should *never* be used for drinking or cooking purposes.

SUG. Explain the action of a cumulative poison.

EXERCISE. Let the student name all the uses of metallic lead that he can call to mind. Also let him name the alloys of lead and their uses.

A good solvent for lead is dilute nitric acid, since the nitrate is a very soluble lead salt. The nitrate and acetate solutions in water are the best ones to use as working solutions.

THE PRINCIPAL COMPOUNDS OF LEAD ARE:—

(*a*) *Lead Oxide* or *Massicot*, PbO, a yellow powder. *Litharge* is an impure form of lead oxide, containing oxides of other metals, as of copper, iron, etc. Both forms are obtained by heating lead in the air. Litharge is used in glazing earthenware, in preparing flint glass, and in the manufacture of *Red Lead* or *Minium*, Pb_3O_4. This last is much used as a pigment, and in steam-pipe fitting.

(*b*) *Lead Acetate*, or Sugar of Lead, $Pb(C_2H_3O_2)_2$, is used in medicine; in the laboratory it is a valuable reagent; in the arts it is used with potassium bichromate, $K_2Cr_2O_7$, for dyeing.

Exp. 140 p. Moisten a strip of white cotton cloth in a solution of lead acetate, and then moisten it in a solution of potassium bichromate. What color is the strip *dyed ?*

(*c*) *White Lead*, 2 to 3 $PbCO_3+Pb(OH)_2$, the principal and best white paint known. It is prepared ("Dutch method") by placing rolls of sheet lead in earthenware vessels containing vinegar or crude acetic acid. These vessels are then piled in tiers, layers of manure or spent tan-bark being placed between. The whole is then covered with manure, which, by its decomposition, furnishes sufficient heat to cause the sheet lead and acetic acid to react and to form the compound $Pb(C_2H_3O_2)_2.2PbO$. This compound is next decomposed by the carbon-dioxide which escapes from the fermenting mass around the vessels. In four or five weeks the process is completed.

In the "French method" white lead is prepared by passing carbon-dioxide through an aqueous solution of litharge in lead acetate.

(*d*) *Galena*, PbS, is a dark, shining solid, crystallizing in cubes and in other forms belonging to the regular system. It is the principal ore of lead.

(*e*) ***Lead Chromate***, or ***Chrome Yellow***, $PbCrO_4$, is a pigment obtained by treating a soluble lead salt with potassium bichromate, $K_2Cr_2O_7$.

(*f*) ***Lead Chloride***, $PbCl_2$, is important as a precipitate met with in the regular course of analysis. It is a crystalline, white solid, *soluble in hot water.*

EXERCISE. Precipitate a dilute solution of lead acetate or nitrate with $K_2Cr_2O_7$. Note the color of the precipitate, and try its solubility in HNO_3 and ammonia. Thus try other precipitants, as HCl, H_2SO_4, $(NH_4)_2S$, KOH, and KI, and test the solubility of the precipitates as before. Tabulate the results and keep them for future reference.

238. Tests for Lead. — 1. Metallic lead is recognized by its lustre, tarnish, streak, and malleability. (See Exp. 136.)

REM. If the student is not sure, he may dissolve a bit of the metal in dilute nitric acid, and test by 2.

2. Lead, in a solution of its salts, is detected by the colors of its precipitates: —

(*a*)	H_2S gives	PbS (black),
(*b*)	$K_2Cr_2O_7$ gives	$PbCrO_4$ (yellow),
(*c*)	$(NH_4)_2CO_3$ gives	$PbCO_3$, $Pb(OH)_2$ (white),
(*d*)	KI gives	PbI_2 (yellow scales),
(*e*)	H_2SO_4 gives	$PbSO_4$ (white).

3. Lead in an unknown solid is detected by reduction on charcoal with sodium carbonate, and, if farther identification be necessary, by 2, after dissolving the bead in nitric acid.

SILVER.

SYMBOL, AG'. — ATOMIC WEIGHT, 108. — SPECIFIC HEAT, 0.0570.
— MELTING-POINT, 1000°.

239. Occurrence. — Silver occurs native in considerable quantities with native copper deposits, but its chief sources are from the lead furnaces, mentioned in Art. 236, and from the following ores: Argentite, Ag_2S; Ruby Silver, Ag_3SbS_3; Silver-Copper Glance, $Ag_2Cu_2S_2$; Horn Silver, AgCl; and other compounds containing silver, copper, antimony, arsenic, and sulphur in varying proportions.

240. Preparation of Metallic Silver. — Exp. 141 P. In a test-tube containing a solution of silver nitrate place a strip of zinc. Fuse the dark-colored deposit on charcoal before the blow-pipe. Try the bead as you tried lead. What differences do you find? Thus reduce silver by means of strips of copper and iron. Write the equations and explain the reactions. Will mercury thus yield *metallic* silver?

Exp. 142 P. Try to prepare silver by the electrolysis of silver nitrate (see Exp. 138). Fuse to a bead on charcoal the substance obtained. Does silver tarnish like lead?

Exp. 143 P. Heat any silver salt, as AgCl, on charcoal before the reducing-flame. Try to oxidize the bead thus obtained, by using the oxidizing flame. Can you thus oxidize lead? Can you separate silver from lead by the blow-pipe?

Exp. 144 P. To a solution of silver nitrate add tartaric acid, $H_2C_4H_4O_6$, and heat. Note the silver mirror deposited on the sides of the test-tube. Is this an instance of oxidation or reduction? What then occurs to the acid?

Exp. 145 P. To a solution of silver nitrate add a little of a solution of chloral hydrate, C_2HCl_3O, H_2O. Make the mixture faintly alkaline with ammonia, and heat. Is a silver mirror again formed on the sides of the test-tube?

QUERIES. In how many ways have you prepared silver? Would the process of reducing silver with zinc be an economical one, provided there were no better processes? Heat the crystals of the Arbor Dianæ (Exp. 134) in an iron spoon. Can you regain the silver, thus separating silver from mercury?

Silver is reduced from its ores in three different ways.

(1) by Cupellation, or Oxidation of lead; (2) by Amalgamation; (3) by Solution and Precipitation.

1. In the lead furnaces metallic silver is obtained together with the lead. This alloy of lead and silver, when molten, is allowed to cool slowly; when the temperature reaches a certain point, most of the lead separates out in crystals, which are removed by means of perforated dippers. In this way an alloy of lead rich in silver is obtained.

Again, in certain localities, where some of the purer ores of silver occur, the crude ore is melted with pure lead; thus a similar alloy is obtained.

The alloy obtained in either case is freed from lead by *cupellation*, *i.e.*, it is strongly heated in bone-ash vessels, called *cupels*, over which a current of air is flowing. At a high temperature the lead is oxidized, while the silver is not changed; upon completion of the process, metallic silver remains in the bottom of the cupel.

QUERY. In what experiment were principles of this process employed?

2. In the *amalgamation* process the ore is ground fine (sometimes first roasted) and mixed with sodium chloride and mercury; copper sulphate is also frequently added. In this way a silver amalgam is obtained. The silver is separated by distilling off the mercury in iron retorts. The mercury is condensed in cool receivers and again employed for the same purpose.

QUERY. What experiment foreshadows this process?

3. In the third process the silver ore is first roasted. If it contains the sulphides of iron and copper, which is frequently the case, the silver is oxidized to the sulphate, Ag_2SO_4, which, by means of water, may be dissolved out from the insoluble oxides of copper and iron formed by

the roasting. From the *solution* of silver sulphate thus obtained metallic silver is *precipitated* by introducing metallic iron.

If the ore does not contain the sulphides of iron and copper, sodium chloride is mixed with the ore before roasting. Silver chloride is obtained, which is then dissolved in sodium thiosulphate. Silver sulphide is next *precipitated* by adding to the thiosulphate *solution* sodium sulphide. Finally the sulphur is driven off by heating the silver sulphide in a muffle furnace.

QUERY. What experiment illustrates these principles?

EXP. 146 P. To a solution of silver nitrate add ferrous sulphate. Do you obtain a precipitate? Is it silver?

QUERIES. Is silver easily reduced from its salts? What substances have been mentioned which are capable of thus reducing silver? Why does silver nitrate blacken the skin or other organic materials? Will a solution of sugar reduce silver?

241. Properties, Uses, and Compounds of Silver.— Silver is one of the precious metals, and has been known and valued since the highest antiquity. It is white, brilliant, and very ductile and malleable. It does not oxidize in the air at any temperature, hence its use in coinage and jewelry.

Silver is readily attacked by ozone, chlorine, bromine, iodine, phosphorus, sulphur, and sulphuretted hydrogen.

QUERIES. Why does silver coin blacken when carried in the pocket with matches? Why do egg and mustard spoons blacken? Why drinking cups used with sulphur waters? What substance is a good solvent for silver sulphide? Explain its action on blackened silverware. What gases from soft-coal grates and from burning illuminating gas blacken silver?

EXERCISE. Name all the uses for which silver is employed.

The best solvent for silver is nitric acid, and silver nitrate is the best salt to use in working solutions.

THE PRINCIPAL COMPOUNDS OF SILVER ARE: —

(*a*) *Silver Nitrate*, $AgNO_3$, or Lunar Caustic. This salt is prepared by dissolving silver in nitric acid. It is extensively used in medicine as an escharotic agent; in photography; in the laboratory as a reagent; as an indelible ink, etc. Sticks of lunar caustic are prepared by fusing the ordinary crystals of silver nitrate and casting the fused mass in moulds.

EXP. 147 P. Moisten a sheet of paper with silver nitrate; dry the paper in the dark; lay upon the prepared paper a fern leaf, a skeleton leaf, or a bit of lace. Cover with a sheet of glass. Expose the whole to sunlight until the sheet is blackened. Now in the dark treat the paper with a solution of sodium thiosulphate, and then wash perfectly clean with pure water. Explain the formation of the "print" obtained. Thus prepare a print from a lantern-slide or a photographer's negative.

(*b*) *Silver-Plating Solution* may be obtained by dissolving silver chloride in an excess of potassium cyanide. The preparation of this substance is shown by the two equations: —

$$1.\ AgNO_3 + NaCl = \underline{AgCl} + NaNO_3.$$

$$2.\ AgCl + 2\,KCy = \underline{AgCyKCy} + KCl.$$

This is used as an electro silver-plating solution. See Gore's *Electro-Metallurgy* for full directions for electro-plating. Also read R. and S., Vol. II., Pt. I., pp. 361–65.

NOTE. The AgCl is freed from the $NaNO_3$ by filtration and washing. The silver potassium cyanide solution with the potassium chloride may be used as a silver electro-plating solution.

(*c*) *Silver Chloride*, AgCl, is important, in that it is a *group precipitate*, obtained by adding hydrochloric acid to a silver salt solution. *This precipitate is soluble in ammonia:* —

$$2\,AgCl + 3\,NH_3 = (NH_3)_3(AgCl)_2\ (?).$$

(*d*) *Silver Bromide*, AgBr, is used in photography, and may be thus prepared: —

$$AgNO_3 + KBr = AgBr + KNO_3.$$

In an impure form silver bromide occurs native.

Exercise. Precipitate a silver nitrate solution with HCl, and test the solubility of the precipitate with NH_3, KCy, $Na_2S_2O_3$, and HNO_3. Thus obtain and try the precipitates with KBr, KI, and KOH or NaOH. Tabulate the results (with colors of precipitates) and preserve them for future reference.

242. Tests for Silver. — 1. Metallic silver is recognized by its lustre and other physical properties.

2. If the student is not sure, he may dissolve a bit of the metal in HNO_3 and add HCl. A white precipitate, insoluble in HNO_3, and soluble in ammonia, indicates silver.

3. Unknown solids may be tested on charcoal with the blow-pipe. The bead may be examined as in 1 and 2.

4. Unknown solutions are tested by adding: —

(*a*) HCl, etc., as in 2;
(*b*) $FeSO_4$, as in Exp. 146;
(*c*) H_2S gas, which gives a black precipitate, Ag_2S, soluble in KCy and strong HNO_3.

5. Silver may be separated from lead by using the oxidizing flame of the blow-pipe as in Exp. 143.

MERCURY.

Symbol, Hg′,″. — Atomic Weight, 200. — Specific Heat, 0.0319. — Melting-Point, − 40°. — Boiling-Point, 357.25°.

243. Occurrence. — Metallic mercury occurs only in very minute globules disseminated through its chief ore, Cinnabar, HgS. Cinnabar occurs in Mexico, California, Spain, Bavaria, China, Japan, and other countries.

244. Preparation. — Exp. 148 p. In a hard glass tube, open at both ends, place a small quantity of vermillion or cinnabar, HgS. Hold the tube somewhat slanting in the Bunsen flame, and heat strongly. Sulphur dioxide fumes escape from the upper end of the tube, while mercury is deposited in the tube in the form of a mirror. Write the equation.

Exp. 149 p. Heat red oxide of mercury, HgO, in a test-tube, and explain what takes place. In what connection have you thus treated HgO?

Exp. 150 p. In a solution of a mercury salt suspend a strip of zinc. In what form do you thus obtain mercury? Thus proceed with a piece of clean copper wire; an iron wire. Do you obtain mercury in both cases? Compare the precipitate obtained by zinc in the mercury salt solution with those precipitates obtained in silver and lead salt solutions.

Exercise. Prepare a table showing the action of copper, zinc, and iron upon the salts of the first group metals.

Query. Can you obtain metallic mercury from its salts by means of reducing agents, such as sugar, chloral hydrate, $FeSO_4$, $SnCl_2$, etc.? Compare by means of a table the results obtained with those obtained with lead and silver salts.

The commercial preparation of mercury is a very simple process. Cinnabar is simply heated in a furnace so constructed that a current of air is passed through the highly heated ore. The sulphur is oxidized to sulphur dioxide; the mercury is vaporized, and afterwards condensed under water in a cooling chamber.

Queries. Why was the tube in Exp. 148 open at both ends? In the next Exp. why could one end of the tube be closed? Which of these experiments illustrates the process for manufacturing mercury?

245. Properties, Uses, and Compounds of Mercury.— Metallic mercury is a silver-white liquid, vaporizing slowly at all temperatures between its freezing-point and boiling-point. Its properties were discovered and discussed by the alchemists, and some of its compounds were found to possess great medicinal properties.

Mercury acts as a poison upon the human system, especially when in the form of vapor.

Metallic mercury is used in constructing thermometers, barometers, and other instruments used in physical measurements. Its amalgams are of great value.

The best solvent for mercury is nitric acid. Solutions of mercurous nitrate, $Hg_2(NO_3)_2$, *and mercuric chloride are good working solutions.*

THE PRINCIPAL COMPOUNDS OF MERCURY ARE:—

(*a*) *Cinnabar*, HgS, an ore of mercury; the artificial sulphide is used as a paint (vermillion).

(*b*) *Red Oxide of Mercury*, HgO, also called *Red Precipitate;* it is used in medicine. This compound is obtained by heating a very intimate mixture of mercury and mercuric nitrate until no red fumes are given off. It may also be obtained as an orange-yellow powder by adding an excess of sodium or potassium hydroxides to the solution of a mercuric salt.

(*c*) *Mercurous Chloride*, or *Calomel*, Hg_2Cl_2, is used in medicine. This substance is prepared by subliming an intimate mixture of mercuric chloride and mercury. It is also obtained when an excess of hydrochloric acid is added to a solution of mercurous nitrate. When thus obtained, it is a *Group Precipitate* which *turns black* with ammonia:—

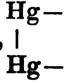
$$Hg_2Cl_2 + 2\,NH_3 = NH_2Hg_2Cl + NH_4Cl.$$

Mercurous chloride is *soluble in nitro-hydrochloric acid.*

(*d*) *Mercuric Chloride*, or *Corrosive Sublimate*, $HgCl_2$, is a

deadly poison; it is used in medicine, and in the laboratory as a reagent. This substance is prepared by subliming a mixture of mercuric sulphate and common salt.

(*e*) *Mercurous Nitrate*, $Hg_2(NO_3)_2$, is often sold fraudulently as a silver-plating solution. This is to be had by treating an excess of metallic mercury with cold, dilute nitric acid. If the acid be in excess, mercuric nitrate, $Hg(NO_3)_2$, is obtained.

It will be seen that mercury forms two compounds with chlorine and two with nitric acid. Were we to examine the entire list of the salts of mercury, we should find numerous other illustrations of this tendency on the part of the metal to form two distinct series of derivatives, of which the two chlorides and two nitrates mentioned are good representatives. The simplest formulae which can be assigned to the two chlorides are HgCl and $HgCl_2$, and to the two nitrates, $HgNO_3$ and $Hg(NO_3)_2$. It would appear from these formulae that in the simpler compounds, HgCl and $HgNO_3$, mercury acts as a univalent element; whereas, in the more complicated compounds, $HgCl_2$ and $Hg(NO_3)_2$, it acts as a bivalent element. It appears more probable, however, that the formulae of the simpler compounds should be doubled, becoming Hg_2Cl_2 and $Hg_2(NO_3)_2$; and perhaps in these compounds the two mercury atoms are united with each other, as indicated thus,  $\begin{matrix}\text{Hg}-\\ |\\ \text{Hg}-\end{matrix}$, forming a bivalent group.

However this may be, it is more common nowadays to write the doubled formulae, and we thus have the two series of mercury compounds corresponding to Hg_2Cl_2 and $HgCl_2$. The former is called mercur*ous* chloride, and the latter, mercur*ic* chloride. The chloride containing the smaller proportion of the acid constituent is designated by the terminal syllable *-ous*, while that chloride which contains the larger proportion of the acid constituent is designated by the syllable *-ic*. The mercurous salts correspond in composition to mercurous chloride. The mercuric salts correspond to mercuric chloride.

Similar series of salts are known in connection with: iron, which gives ferrous and ferric salts; copper, which gives cuprous and cupric salts; and many other metals. The most marked cases are those of mercury, iron, and copper.

Only the mercurous salts are precipitated in the first group. The mercuric salts are thrown down in the second group.

Exercise. With a solution of a mercurous salt try the precipitants HCl, H_2S, KI, and KOH. Try the solubility of each precipitate in HNO_3, and in nitro-hydrochloric acid. Thus proceed with a mercuric salt; make a table comparing the results.

246. Tests for Mercury and the Mercury Compounds. — 1. Metallic mercury is readily recognized by its physical properties.

2. An unknown solid is tested for mercury by heating it in a test-tube with anhydrous sodium carbonate, Na_2CO_3. A mirror of metallic mercury is formed on the sides of the test-tube.

3. An unknown solution is tested for mercury by adding: —

(*a*) HCl. If a white precipitate be formed, filter it out and moisten it on the filter-paper with ammonia. If the precipitate turns black, mercury in the *mercurous* condition is present.

(*b*) Through the filtrate from (*a*) pass hydrogen sulphide. Mercury, in the *mercuric* condition, gives a black precipitate, which is to be tested farther by dissolving it in nitro-hydrochloric acid, and evaporate to expel the excess of acid; to this solution add stannous chloride, $SnCl_2$: —

$$HgCl_2 + SnCl_2 = \underline{\underline{Hg}} + SnCl_4.$$

The mercury thus obtained appears (usually after some time) as a finely-divided, black precipitate.

4. A copper wire in a solution containing a mercury salt is soon coated with a silver-white deposit.

5. A solid may be dissolved in nitro-hydrochloric acid, and the solution directly tested by $SnCl_2$, or by 4.

247. To separate and identify Lead, Silver, and Mercury (Hg_2). — 1. To a solution containing salts of these three metals add HCl; the compounds $PbCl_2$, AgCl, and Hg_2Cl_2 are thus obtained together in the form of a precipitate. Filter and wash this precipitate with a *little cold water*.

Note. Lead is not completely precipitated by HCl; consequently some lead usually passes over into the second group.

2. Add *much hot water* to the precipitate as it lies on the filter-paper. The lead chloride, $PbCl_2$, is thus dissolved, and will now run through the filter-paper. Collect this solution in a beaker, and test for lead by Art. 238, 2.

3. The undissolved precipitate on the filter-paper now consists of AgCl and Hg_2Cl_2. The silver chloride, AgCl, may now be dissolved out by adding a little ammonia. Collect the solution, $(NH_3)_3(AgCl)_2$, as it runs through, and test for silver by acidulating it with nitric acid; AgCl is again precipitated: —

$$(NH_3)_3(AgCl)_2 + 3\,HNO_3 = 2\,AgCl + 3\,NH_4NO_3.$$

Note. The formation, in this connection, of the white precipitate, AgCl, upon adding nitric acid, is sufficient to identify silver; but in case the precipitate be plentiful, a bead of metallic silver may be had, as in Art. 242, 3.

4. At the same time that the silver chloride dissolves in ammonia, the mercurous chloride, Hg_2Cl_2, turns black (245, *c*) and remains on the filter-paper. This blackening, in this connection, is a sufficient indication that mercurous compounds are present. A farther test, by 246, 5, may be employed, however, if desirable.

248. To separate Mercury, Lead, and Silver by the Blow-Pipe. — Exp. 151 p. Make an amalgam of silver, as in Exp. 134. Also make an amalgam of lead by warming and rubbing bits of lead and mercury in an evaporating-dish; mix the two amalgams; you thus have a compound of metallic mercury, lead, and silver.

1. Carefully heat a bit of this compound on charcoal in the *reducing*-flame until you think you have driven off the mercury. Dissolve the residue in dilute nitric acid, and test by Art. 247. If the separation of the mercury was complete, you will obtain tests for lead and silver only.

2. Heat another bit of the compound on charcoal in the *oxidizing* flame. You may thus drive off the mercury and oxidize the lead, leaving a bead of metallic silver. Dissolve this bead in nitric acid, and try for silver, lead, and mercury by Art. 247. If the separation of mercury and lead was complete, you will obtain a test for silver only.

Note. In case the amalgam, when heated as in 1, spits out and is lost, this step may be accomplished by carefully heating and shaking a fresh portion in an iron spoon.

249. Reactions in Group I. — Balance these equations. What principles do they illustrate?

(1) $Pb + HNO_3 = Pb(NO_3)_2 + NO + H_2O.$

(2) $Ag + HNO_3 = AgNO_3 + NO + H_2O.$

(3) $Hg_2 + \underset{\text{(dilute)}}{HNO_3} = Hg_2(NO_3)_2 + NO + H_2O.$

(4) $Pb(NO_3)_2 + HCl = \underline{PbCl_2} + HNO_3.$

(5) $AgNO_3 + HCl = \underline{AgCl} + HNO_3$.
(6) $Hg_2(NO_3)_2 + HCl = \underline{Hg_2Cl_2} + HNO_3$.
(7) $PbCl_2 + H_2O =$ Sol. of $PbCl_2$.
(8) $PbCl_2 + K_2CrO_4 = \underline{PbCrO_4} + KCl$.
(9) $AgCl + NH_3 = (NH_3)_3(AgCl)_2$.
(10) $(NH_3)_3(AgCl)_2 + HNO_3 = \underline{AgCl} + NH_4NO_3$.
(11) $Hg_2Cl_2 + NH_3 = \underline{NH_2Hg_2Cl} + NH_4Cl$.
(12) $NH_2Hg_2Cl + NOCl_2 + Cl + H_2O = HgCl_2 + NO_2$.
(13) $HgCl_2 + SnCl_2 = Hg + SnCl_4$.

SUG. The precipitates are underscored. Let the student determine which of the substances on the right of the sign = are gases.

MODEL RECITATION. Equations 1, 4, 7, and 8 illustrate the reactions previously described in lead. No. 1 shows how lead is dissolved; $Pb(NO_3)_2$ is the substance in solution; NO is a gas. No. 4 shows the precipitation of lead with HCl. $PbCl_2$ is the precipitate. No. 8 shows the distinctive test for lead ($PbCrO_4$ being yellow) which was separated from silver and mercury by No. 7. Give the name and the formula of each compound.

EXERCISES.

1. Observe that different products are obtained when some substances react, depending upon which substance is in excess. Thus, if Hg be in excess, silver amalgam is obtained in Exp. 134, while an excess of $AgNO_3$ gives pure silver. What other instances have been given?
2. Read R. and S., Vol. II., Pt. I., pp. 388 to 392, for different processes of preparing mercury.
3. Expose some freshly prepared AgCl to the action of sunlight. What changes in color occur?
4. Compute the atomic heats and atomic volumes of lead, silver, and mercury.

NOTE. The expression "*group precipitate*," as used in the text in connection with a single metallic salt, signifies the precipitate of that metal obtained by the group reagent.

CHAPTER XVI.

THE SECOND GROUP METALS.

250. The second group metals are those the sulphides of which are insoluble in dilute acids. These metals are separated from all others by removing the first group metals with hydrochloric acid, after which hydrogen sulphide, H_2S, is passed through the acidulated solution.

Note. Tellurium and Selenium, which are precipitated with these metals, have already been described. Lead which has not been fully removed from the first group also appears in this group.

The metals of this group exhibit many kindred properties. Their oxides, excepting those of arsenic, are nearly insoluble in water; they do not decompose water except at high temperatures, and then but four, viz., bismuth, antimony, tin, and molybdenum, give this reaction to any considerable extent; all the commonly occurring metals form soluble nitrates (excepting antimony and tin, which form oxides) when treated with nitric acid; all are readily reduced to the metallic state when heated on charcoal in the reducing-flame.

In deference to some requirements in analysis, we may divide the common metals of this group into two divisions. The metals of the first division yield sulphides which are soluble in *yellow ammonium sulphide*, $(NH_4)_2S_2$, while the sulphides of the second division are insoluble in that reagent. Let us distinguish these divisions by the letters A and B; then each division is as follows: —

DIVISION A
Arsenic.
Antimony.
Tin.

DIVISION B
Mercury (in mercuric salts).
Lead.
Bismuth.
Copper.
Cadmium.

NOTE. The yellow ammonium sulphide for the purposes mentioned in this chapter may be prepared by gently warming in a test-tube a little reagent ammonium sulphide, $(NH_4)_2S$, with a small quantity of flowers of sulphur. The reagent sulphide, upon standing, also changes to the yellow variety.

DIVISION A.

ARSENIC.

SYMBOL, $As^{iii, v}$. — ATOMIC WEIGHT, 75. — SPECIFIC HEAT, 0.0822. — MELTING-POINT, 356°.

251. Occurrence. — In nature arsenic occurs free in kidney-shaped masses, which usually may be split up into thin laminæ or leaves; but commercial arsenic is obtained chiefly from some of the following ores: Iron Arsenide, $FeAs_2$; Nickel Arsenide, NiAs; Mispickel, $(FeS)_2As$; Realgar, As_2S_2; Orpiment, As_2S_3; and from Arsenic Trioxide, As_2O_3, combined with lead, calcium, and cobalt as arsenites.

252. Preparation. — EXP. 152 P. Make a pellet of arsenic trioxide, As_2O_3 (commonly known as "arsenic"), with powdered charcoal and a drop or two of water. Place the pellet in the bottom of a hard glass test-tube, and heat gently to expel the water. Now insert a loosely-fitting stopper (made of chalk) nearly down to the pellet, which is then to be heated to redness. Arsenic is freed and vaporized; the vapors condense, above the chalk, on the sides of the test-tube, forming a metallic mirror.

EXP. 153 P. Heat any arsenic compound, as As_2O_3, on charcoal before the reducing-flame. Arsenic is freed in form of a vapor which has an odor somewhat resembling *garlic*.

Similarly treat a bit of metallic arsenic. Do you obtain the same odor? How do you now know that arsenic was freed by heating As_2O_3?

Commercial arsenic is prepared by heating its ores, especially mispickel and orpiment, in earthen vessels or tubes. The arsenic is driven off in vapors, which are condensed in sheet iron tubes or condensers.

To purify the arsenic thus obtained it is sublimed with charcoal, when it condenses in rhombohedral crystals possessing a bright metallic lustre.

253. Properties, Uses, and Compounds of Arsenic. — Arsenic is a solid substance possessing a steel-gray color and a metallic lustre. When heated under ordinary pressure, it seems to vaporize without melting, at 356°; under greater pressure, however, it may be obtained in a liquid state.

As previously noted, arsenic stands midway between the metals and non-metals; in its chemical compounds and chemical deportment it is closely allied to phosphorus on the one hand, while, on the other hand, the physical properties of arsenic and its compounds bear a close resemblance to those of antimony.

Arsenic oxidizes quite readily in warm, moist air, forming a dark substance (probably a low oxide) known as *fly powder.* When strongly heated in oxygen, arsenic burns with a white light, forming arsenic trioxide, As_2O_3. With oxygen and hydrogen, arsenic forms the acids arsenious acid, H_3AsO_3(?), and arsenic acid, H_3AsO_4, which closely resemble the corresponding acids of phosphorus.

The vapors of arsenic possess a strong odor resembling garlic. Both arsenic and its soluble salts act as deadly poisons when taken into the system, and even arsenical vapors produce the symptoms of arsenic poisoning when inhaled or absorbed through the pores of the skin.

The best antidote for arsenic is freshly prepared ferric hydroxide, $Fe_2(OH)_6$, made by adding ammonia to a solution of ferric chloride, Fe_2Cl_6. The ferric hydroxide is filtered out and washed, when it is ready for use. Magnesia, MgO, is also an antidote; both these substances form insoluble compounds with the arsenic, thus preventing its absorption by the system. An emetic, such as a teaspoonful of mustard in a cup of warm water, should soon follow the antidote, and that in turn should be followed by castor oil.

Arsenic is dissolved by nitro-hydrochloric acid or by chlorine water: —

$$2\,As + 5\,Cl_2 + 8\,H_2O = 2\,H_3AsO_4 + 10\,HCl.$$

A good working solution of an arsenite can be made thus: —

$$As_2O_3 + 6\,NaOH = 2\,Na_3AsO_3 + 3\,H_2O\ (+\text{ an excess of }NaOH).$$

THE PRINCIPAL COMPOUNDS OF ARSENIC ARE: —

(*a*) *Arsenic Trioxide*, As_2O_3. This oxide is sometimes called arsenious anhydride, and is usually sold in drug stores as "arsenic." This a white crystalline powder, used for destroying vermin, as a medicine, and in taxidermy as a dryer and antiseptic. *Arsenious Acid*, H_3AsO_3, has not been isolated; from it are derived the arsenites. All the soluble arsenites are poisonous.

(*b*) *Arseniuretted Hydrogen* or *Hydrogen Arsenide*, AsH_3, which is an exceedingly poisonous, inflammable gas evolved by treating any compound of arsenic with nascent hydrogen. The same apparatus used for hydrogen sulphide may be employed for this purpose. This gas is to be had by placing in the test-tube any arsenic salt together with metallic zinc and dilute sulphuric acid. This gas is generated in making the "spot test" (Art. 254) for arsenic, and great care must be used not to inhale any of it. Allow the acid and zinc to work until the apparatus is free from air before adding the arsenic compound; the gas escaping from the jet should be immediately ignited.

(*c*) *Scheele's Green* or *Copper Arsenite*, $CuHAsO_3$. This compound is to be had by adding an aqueous solution of arsenic trioxide to an ammonia-copper sulphate solution; this latter solution is prepared by adding ammonia to a solution of copper sulphate until the precipitate, which is at first formed, dissolves.

Schweinfurth's Green is a copper aceto-arsenite, $(CuOAs_2O_3)_3$-$Cu(C_2H_3O_2)_2$. Both of these compounds are used as pigments, and are sold under the name of *Paris Green*. Gardeners use them as anti-insect powders. Wall paper frequently owes its green tints to the presence of one of these compounds; such paper is dangerous, sometimes giving rise to aggravated cases of arsenic poisoning. It seems that such papers give off arsenical vapors or dust, which are disseminated through the air and absorbed by the pores of the skin and by the lungs.

(*d*) *Arsenic Pentoxide*, As_2O_5, and *Arsenic Acid*, H_3AsO_4. The first is prepared by dissolving arsenic in strong hot nitric acid, after which the solution is first evaporated and then fused at a dark-red heat. Arsenic acid is obtained by treating arsenic with chlorine as previously explained. From this acid we obtain the *arsenates*.

(*e*) *Arsenious Sulphide*, As_2S_3, is the *group-reagent precipitate*, and may be had by treating any soluble arsenic salt with hydrogen sulphide. This is a yellow powder *soluble in yellow ammonium sulphide*, $(NH_4)_2S_2$.

(*f*) *Sodium Arsenate* is used to remove the mordant in calico printing. The impure form thus employed is made by dissolving arsenic trioxide in sodium hydroxide, after which sodium nitrate is added; the solution is then evaporated to dryness. (Read R. and S., Vol. II., Pt. I., p. 125.)

254. Tests for Arsenic and its Compounds.—1. Metallic arsenic is to be distinguished by its physical properties and by its giving a garlic odor when heated in the reducing-flame on charcoal.

2. Solutions or solids are best tested by the "spot or mirror test." The solid or solution is first treated with a crystal of potassium chlorate and hydrochloric acid to oxidize the arsenic (if any be present) to arsenic acid. The excess of chlorine is expelled, and the prepared solution is now treated with arsenic-free zinc and dilute sulphuric acid. Hydrogen arsenide is thus evolved. The escaping gas is delivered through a jet and is ignited. Now hold a piece of cold porcelain in the flame. Arsenic if present is deposited on the porcelain as a bright steel-gray spot or mirror.

Make several spots, and make sure that they are arsenic, thus:—

(*a*) Try one spot with a drop of yellow ammonium sulphide; it turns yellow.

(*b*) Try another with a drop of hydrochloric acid; *it does not dissolve.*

(*c*) Add to another a drop of a solution of bromine or chlorine in potassium hydroxide; it dissolves.

(*d*) Try another with hot nitric acid; *it dissolves clear.* Then to this clear solution add a drop of silver nitrate; no change in color occurs. Now treat the solution with ammonia vapor, which may be forced against the solution by blowing through a blow-pipe across the mouth of an uncorked ammonia bottle; *the solution turns brick-red or yellow.* You may now be assured that arsenic in some form is present.

3. *To distinguish an arsenate from an arsenite.* Make a

clear solution of magnesium sulphate, $MgSO_4$, ammonia, and ammonium chloride, NH_4Cl. To this clear solution add the unknown solution, a portion of which has been found to contain arsenic by 2. A white precipitate (in the absence of phosphates) indicates an arsenate. An arsenite gives a white precipitate with $MgSO_4$ which is soluble in ammonia and NH_4Cl. A solution of arsenic trioxide in an excess of sodium hydroxide, when treated with copper sulphate, gives a blue solution from which a red precipitate of Cu_2O is thrown down on boiling.

Note. Any arsenic compound in solution gives a yellow precipitate, As_2S_3, with H_2S.

ANTIMONY.

Symbol, $Sb^{''',v}$. — Atomic Weight, 120. — Specific Heat, 0.0523. — Melting-Point, 425°.

255. Occurrence. — Native antimony occurs in small quantities as scaly masses which are contaminated with iron, silver, etc.; but its chief source is Stibnite, Sb_2S_3. Other ores of less importance also occur.

256. Preparation. — Exp. 154 p. Make a pellet of a thoroughly pulverized antimony compound, as stibnite, Sb_2S_3, with potassium cyanide or with sodium carbonate and a drop of water. Heat on charcoal in the reducing-flame; a bright metallic bead of antimony is obtained. Try the malleability, etc., of this bead as you did of the lead or silver bead. In comparison, how does it behave?

Exp. 155 p. Pulverulent antimony, or *antimony black*, may be prepared by placing a zinc strip in a solution of antimony chloride, $SbCl_3$ (see Art. 257, (c)). How does the precipitate compare with those thus obtained in the first group metals? Preserve this powder for future use.

Commercial antimony is prepared from stibnite. The crude ore is first melted in vessels the bottoms of which are perforated by small openings. The sulphide is melted and runs through these openings nearly pure. The sulphide is next melted with metallic iron, which combines with the sulphur, leaving the antimony free and ready to be drawn off in a molten condition.

By another process the sulphide is converted into an oxide in a reverberatory furnace. The oxide is then reduced by heating it with charcoal or some other reducing agent.

The antimony of commerce often exhibits a stellated surface, which is obtained by allowing the purified molten metal to cool slowly.

257. Properties, Uses, and Compounds of Antimony. — Antimony is a bluish-white metal, so brittle that it may be finely pulverized. It tarnishes slowly in warm, moist air and burns with a white light when heated to redness in the air, forming the trioxide, Sb_2O_3. It vaporizes at a white heat in the absence of oxygen.

Metallic antimony is used principally in making alloys, to which it imparts the property of hardness and that of expansion when cooling from a molten state. Hence it is extensively employed in manufacturing type-metal.

Antimony is also used in many pharmaceutical preparations. That form of antimony which is obtained in Exp. 155, and which is an article of commerce, is employed to impart a metallic surface to plaster casts. It is also used as a medicine for horses.

Exp. 156 p. Coat a small plaster of paris image with antimony black, and polish until the surface assumes a metallic lustre.

With hydrogen and oxygen, antimony forms both acids and bases. With acids it forms salts, in which it plays the part of a trivalent metal, as in antimony sulphate, $Sb_2(SO_4)_3$. It also forms basic salts, in which the group SbO, which is univalent, takes the place of one atom of hydrogen. These are called antimonyl salts. Antimonyl sulphate, $(SbO)_2SO_4$, may serve as an example. The principal acid of antimony is antimonic acid, H_3SbO_4, which closely resembles phosphoric and arsenic acids.

The best solvent for antimony is hot nitro-hydrochloric acid, and the salt thus obtained ($SbCl_3$) *is a good solution for working purposes.*

THE PRINCIPAL COMPOUNDS OF ANTIMONY ARE: —

(*a*) The oxides, Sb_2O_3, Sb_2O_4, and Sb_2O_5, which give rise to a series of acids similar to those of phosphorus. (Art. 220.)

Antimonic Acid, H_3SbO_4, is obtained by oxidizing antimony in nitric acid. None of these acids are employed for industrial purposes, although antimonic acid was formerly used as a medicine.

(*b*) *Tartar Emetic*, $C_4H_4KSbO_7$, which is used in medicine. It is prepared by dissolving antimony trioxide, Sb_2O_3, in cream of tartar or potassium tartrate, $KHC_4H_4O_6$.

(*c*) *Butter of Antimony*, *Antimony Trichloride*, $SbCl_3$. This is prepared by dissolving antimony trisulphide, Sb_2S_3, in hydrochloric acid. It is used in staining iron or steel utensils, such as gun-barrels.

(*d*) *Stibnite*, *Antimony Trisulphide*, Sb_2S_3, which is one of the antimony ores and is of a dark-gray color. That which is obtained by precipitating an antimony salt with hydrogen sulphide is an orange-colored powder. It is a *group-reagent precipitate* insoluble in dilute acids, *soluble in ammonium sulphide*. The *pentasulphide*, Sb_2S_5, resembles the trisulphide.

(*e*) *Hydrogen Stibide*, SbH_3. This is an inflammable gas used in the "spot test" for antimony. This is obtained from an antimony salt by treating it with zinc and sulphuric acid, as in preparing AsH_3, Art. 254, 2.

GENERAL NOTE. Antimony and its salts are poisonous when taken internally, but they are neither so dangerous nor so active as arsenic and its compounds.

258. Tests for Antimony. — 1. Solids containing antimony may be tested in the reducing-flame with sodium carbonate on charcoal. A silver-white, brittle bead is obtained.

2. A very delicate test for antimony, free or combined, is the "spot test." Make several spots by directly treating the substance with zinc and dilute sulphuric acid. These spots are distinguished from arsenic spots by the color. Those of antimony are black or velvety-brown. More certain distinctions are as follows: —

(*a*) The antimony spot with yellow ammonium sulphide turns *orange*.

(*b*) With hot nitric acid turns white.

(*c*) In a solution of bromine or chlorine in potassium hydroxide it is *insoluble*.

(*d*) The white spot, formed in (*b*), treated with silver nitrate and ammonia fumes gives *no color;* but when a drop of ammonia solution is added, the spot turns *black*.

3. Upon addition of water to the solution of an antimony salt acidulated with hydrochloric acid, a portion of the antimony is precipitated as a basic salt soluble in tartaric acid. (See Art. 267, 2.)

NOTE. H_2S forms an *orange*-colored precipitate, Sb_2S_3 or Sb_2S_5, with any antimony compound in solution.

SUG. See *Chemical News*, June 5, 1885, p. 267, and June 19, 1885, p. 292, for some delicate tests for antimony.

TIN.

SYMBOL, $Sn^{ii, iv}$. — ATOMIC WEIGHT, 118. — SPECIFIC HEAT, 0.0548. — MELTING-POINT, 230°.

259. Occurrence.—Small quantities of tin occur native. Its chief ore is Tin Stone, Cassiterite or stannic oxide, SnO_2. This ore occurs in veins in the older schistose and crystalline rocks, and also as nodules or "stream tin" in the beds of rivers traversing the above-mentioned rocks.

The principal tin mines of the world are in Cornwall (England), Australia, Bolivia, and Peru. The mines of Cornwall are the oldest tin-mines known; they were probably worked as far back as during the Bronze Age.

260. Preparation. — EXP. 157 P. Into a solution of a tin salt place a strip of zinc. What results?

EXP. 158 P. Make a paste of a tin salt with solid potassium cyanide, KCy, and a drop of water. Heat this paste on charcoal before the reducing-flame. Small beads of tin are thus obtained with great difficulty. (See Art. 262, 2, for test for tin.)

The first step in its preparation for commerce is to crush the ore and to remove as many impurities as possible by washing. The ore is then roasted in revolving, inclined cylinders through which a continuous blast of air and flame are passing. In this way volatile substances, such as arsenic and sulphur, are driven off, while other impurities are oxidized. The roasted ore is now washed again, and is thus obtained quite pure. It is now reduced to metallic tin by mixing it with anthracite and heating it in a blast-furnace.

The metal is next drawn off and further purified by *liquation*, *i.e.*, it is gradually melted in a reverberatory furnace; the pure tin is more fusible than its alloys, which are present, and melts first. It is then drawn off and stirred with poles of green wood; a dross separates out and is removed. In this way the tin is brought to a state of great purity.

PROPERTIES, USES, AND COMPOUNDS OF TIN.

261. Tin is a white, lustrous metal which is quite permanent in the air at ordinary temperatures and which, in the absence of oxygen, can be vaporized at a white heat. It is very malleable, and is extensively used in the form of thin sheets as *tin foil.* When bent or bitten, bar-tin emits a crackling sound, supposed to be due to the motion of its particles over one another; this goes to show that solid masses of tin probably assume a granular structure.

Tin can be obtained in a crystalline form in different ways: (1) Melt it, and allow the molten mass partially to cool; pour off the liquid portion, when prismatic crystals of tin remain. (2) Decompose a chloride of tin, as $SnCl_2$ or $SnCl_4$, by means of a weak galvanic current. (3) Make a solution of a chloride of tin alkaline, and insert a bright strip of zinc.

Since tin is quite readily reduced from its ores, it has been known from an early time. Its uses are many and its alloys are important.

QUERIES. What is "Block Tin"? What is tin plate, and how is it made? What are the uses of metallic tin?

Tin as a base yields two series of salts, — the stannous and the stannic salts. These are well typified by the chlorides $SnCl_2$ and $SnCl_4$.

The tin acids yield two series of salts of small importance, — the stannates and the metastannates.

The best solvent for tin is hydrochloric acid, stannous chloride, $SnCl_2$, *being the salt produced. Nitro-hydrochloric acid (with excess of* HCl) *dissolves tin, forming stannic chloride,* $SnCl_4$. *These are good working solutions.*

THE PRINCIPAL TIN COMPOUNDS ARE: —

(*a*) *Tin Stone, or Cassiterite*, SnO_2; this is the principal ore of tin.

Stannic Acid, H_2SnO_3, may be supposed to originate thus: —

$$SnO_2 + H_2O = H_2SnO_3.$$

In practice this acid is obtained when calcium carbonate is treated with an excess of stannic chloride. One of the salts of this acid, sodium stannate, Na_2SnO_3, is largely used (as "preparing salts") in calico printing.

Metastannic Acid probably has the formula $H_{10}Sn_5O_{15}$. Both these acids form salts chiefly with the metals of the fifth group.

(*b*) *Stannous Chloride*, $SnCl_2$, and *Stannic Chloride*, $SnCl_4$. These salts are used as reagents in the laboratory. How are they made?

(*c*) *Stannous Sulphide*, SnS, which is a brown powder, while *Stannic Sulphide*, SnS_2, is a yellow one. These are the *group-reagent precipitates*, thrown down by hydrogen sulphide in acid solutions; they are *soluble in yellow ammonium sulphide.*

QUERY. If the solution be a stannic salt, which sulphide is obtained? A stannous salt?

262. Tests for Tin. — 1. Metallic tin is recognized by its lustre and by the crackling sound when bent or bitten.

2. An unknown solid is tested by the blow-pipe, Exp. 158. If the oxidizing flame be used, a coating of stannic oxide, SnO_2, is formed upon the charcoal around the assay. This coating is *pale yellow* when hot, *white* when cold.

3. A solid insoluble in water is dissolved in hydrochloric acid, and mercuric chloride, $HgCl_2$, is added (see Art. 246).

NOTE. At first a white precipitate is obtained, if a stannous salt be present; this soon turns gray and then (usually after some time) black, when metallic mercury is found to have been precipitated. The white precipitate is probably Hg_2Cl_2. Write the equation. This reaction is of importance, since by it we may identify both tin and mercury.

4. An unknown solution is tested by adding: —

(*a*) $HgCl_2$ (see 3).

(*b*) H_2S (see Art. 261 (*c*)).

(*d*) Ammonia and a zinc strip (Art. 261).

QUERY. How can you distinguish between a stannous and a stannic salt?

263. To separate and identify Arsenic, Antimony, and Tin. — There is no simple method which is at the same time very accurate. A fairly good one is the following: Bring the precipitate which contains the sulphides of arsenic, antimony, and tin into a small flask, and boil with concentrated hydrochloric acid as long as the odor of hydrogen sulphide can be detected. The sulphides of antimony and tin are dissolved, while the sulphide of arsenic remains undissolved. Filter and wash, and then treat the undissolved substance with hydrochloric acid and potassium chlorate. It is thus converted into arsenic acid, which may be detected by means of the reactions given in Art. 254, 3. Test also for arsenic by

(*a*) The spot test (Art. 254, 2),

(*b*) Hydrogen sulphide (a yellow precipitate).

The solution containing antimony and tin is treated with zinc, which reduces the compounds to the metallic state. After a time pour off the solution, wash the residue with water, and treat with hydrochloric acid. Only the tin is dissolved. It may be detected by means of mercuric chloride (see Art. 262, 3). Examine the residue and convince yourself that it is antimony by

(*a*) The spot test,
(*b*) Hydrogen sulphide (an orange-colored precipitate).

SUG. Write the equations for the steps involved.

DIVISION B.

The metals of this division of the second group are those whose sulphides are not soluble in yellow ammonium sulphide.

BISMUTH.

SYMBOL, Bi'''. — ATOMIC WEIGHT, 210. — SPECIFIC HEAT, 0.0305. — MELTING-POINT, 270°.

264. Occurrence. — Bismuth is a comparatively rare metal. It usually occurs native, but it is always contaminated with a small percentage of other metals, such as iron, copper, lead, silver, etc.

Of its ores Bismuth Ochre, Bi_2O_3, is the principal one. Bismuthite, Bi_2S_3, ranks next in importance. Most of the bismuth of commerce comes from Saxony.

265. Preparation. — EXP. 159 P. Make a pellet of any bismuth compound with sodium carbonate and a drop of water. Heat it in the reducing-flame on charcoal. Try the bead as you did those of lead, silver, etc. What difference do you find? Treat the bead with the oxidizing-flame. Note the coating on the charcoal. This coating, Bi_2O_3, is characteristic.

EXP. 160 P. Into a solution of bismuth chloride, $BiCl_3$, place a zinc strip, and proceed as usual. Try the same salt with the galvanic current.

Bismuth can be extracted incompletely from its ores by fusion; the extraction can be made complete by roasting them first and afterward fusing them with iron, slag, and charcoal. The crude bismuth thus obtained is purified by melting it at the lowest possible temperature on an inclined plane; the molten metal runs slowly down the plane while the impurities remain behind.

Commercial bismuth is also prepared as in Exp. 160.

266. Properties, Uses, and Compounds of Bismuth. — Metallic bismuth is not employed in a pure state in any of the arts. It is chiefly used in alloys and in making pharmaceutical preparations; nearly 25,000 kilograms are thus consumed annually.

Bismuth is a hard, brittle metal of a grayish-white color with a distinct tinge of red. It oxidizes but slowly in the atmosphere, but the gases of the laboratory cause it quickly to tarnish.

It expands during solidification, and it imparts this property to its alloys, which are, on this account, used in making delicate castings. Many of the alloys of bismuth, especially those with tin, lead, and cadmium, melt at very low temperatures (see Art. 230). These "fusible metals" or alloys are used in stereotyping and electrotyping; they are also used as solders and for making safety plugs for steam boilers.

SUG. Explain the use of the safety plug.

Bismuth, like antimony, forms two kinds of salts, those in which its atom takes the place of three atoms of hydrogen, as in bismuth nitrate, $Bi(NO_3)_3$, and those in which the group BiO, called bismuthyl, takes the place of one atom of hydrogen, as in the salt $(BiO)(NO_3)$. Salts of the former class are decomposed by water and transformed into salts of the latter class, which are known usually as basic salts.

An acid called bismuthic acid, and supposed to have the formula $HBiO_3$, has been described; but very little is known regarding it or its salts.

The best solvent for bismuth is nitric acid. Hydrochloric acid also reacts feebly with this metal. The solutions thus obtained are good working solutions.

THE PRINCIPAL BISMUTH COMPOUNDS ARE AS FOLLOWS:

(*a*) Of the *Bismuth Oxides*, Bi_2O_2 and Bi_2O_3 are the principal ones. Of these two the trioxide Bi_2O_3 is the more important. It is the chief ore of bismuth, and is used as a pigment.

(*b*) *Bismuth Nitrate*, $Bi(NO_3)_3 + 3H_2O$, is obtained by dissolving the metal in nitric acid.

The *Sub-nitrate of Bismuth*, $BiO . NO_3, H_2O$ (of the pharmacopœia), is prepared by precipitating bismuth nitrate by the addition of water to the solution. The sub-nitrate is used in medicine as a remedy for cholera and dysentery. It is also used as a cosmetic, under the names of *Blanc d'Espange* and *Blanc de Fard*. It is further used in glazing porcelain, to which it imparts an iridescent surface. This salt is a white powder, now known as *Bismuth Basic Nitrate*.

(*c*) *Bismuthite*, Bi_2S_3, is an ore of bismuth and the *group-reagent precipitate*. It is obtained from an acid solution of a bismuth salt by passing through it hydrogen sulphide. It is soluble in hot nitric acid.

267. Tests for Bismuth.—1. Unknown solids are tested for bismuth by the blow-pipe. When the bead is treated with the oxidizing-flame, Bi_2O_3 is formed, and the charcoal is coated orange-yellow while hot, lemon-yellow when cold. The edges of the coat are bluish-white when cold.

2. A solution is tested by adding:—

(*a*) Water, which yields a basic salt, as a *white precipitate insoluble in tartaric acid.* (See Art. 258, 3.)

(*b*) H_2S, a black precipitate, Bi_2S_3, soluble in HNO_3.

(*c*) Ammonia, a *white* precipitate, $Bi(OH)_3$.

(*d*) $K_2Cr_2O_7$, a *yellow* precipitate $(BiO)_2Cr_2O_7$, which is insoluble in KOH, a distinction from lead.

(*e*) KI in acid solution gives BiI_3, a *brown*, unstable precipitate soluble in an excess of HCl.

COPPER.

SYMBOL, $Cu^{\prime, \prime\prime}$. — ATOMIC WEIGHT, 63. — SPECIFIC HEAT, 0.0952. — MELTING-POINT, 1090°.

268. Occurrence. — Copper occurs native in large quantities, and the commercial metal is obtained principally from this source. The most plentiful deposits are found in upper Michigan, where masses of the pure metal weighing many tons have been found. It occurs in sheets or veins, intersecting red sandstone and trap rocks, but the largest deposits are found as granular masses mixed through a rocky matrix. Native copper also occurs in many other localities, and nearly every deposit is silver bearing.

The ores of copper occur plentifully and are widely distributed. The principal ores are: Cuprite, Cu_2O; Copper Glance, Cu_2S; Malachite, $CuCO_3 + Cu(OH)_2$; Azurite, $2\,CuCO_3 + Cu(OH)_2$; and Copper Pyrites, $CuFeS_2$.

The argentiferous copper ores of the Rocky Mountains, especially those of Montana, have of late years furnished a large amount of the copper in the market, at times so reducing the price of the metal as to necessitate a temporary suspension of the mines till a higher price would render the mining and smelting of the ores more profitable.

269. Preparation. — Native copper usually requires little treatment except smelting; but the reduction of its ores to obtain commercial copper is a somewhat complicated process of minor interest, at present, to the American student. From its soluble salts copper may be obtained by precipitation and by electrolysis.

Exp. 161 p. Place a bright strip of iron in a solution of copper sulphate, $CuSO_4$. It is soon coated with a film of metallic copper. Thus try a strip of zinc. What result? Try two strips at once, one of zinc and one of iron. What result? Does the iron increase in weight owing to the deposit of copper? In what ratio?

We have many familiar examples of the reduction of copper from the solution of its salts. In gravity batteries the copper plates are soon covered with a deposit of copper; in electrotyping, a metallic film is deposited upon a wax mould of the type, and this film is afterward strengthened by a fusible metal (it is thus that the plates were prepared from which these pages were printed); the hypophosphites, when heated with the solution of a copper salt, reduce metallic copper; and the following metals will give metallic copper with a solution of a copper salt: iron, zinc, cobalt, nickel, lead, cadmium, bismuth, and tin.

270. Properties, Uses, and Compounds of Copper. — Owing to its abundance in the native state, copper was probably the first metal used by man. The prehistoric copper miners of Lake Superior employed the rudest methods imaginable for mining and working copper. They confined their operations chiefly to the sheet-like veins which were visible at the surface. Owing to the dip of the rocks only the edge of the sheet was within their reach. They built wood fires upon the rocks until the stone would crumble and leave a narrow ribbon of copper exposed; then, by means of a stone from the lake shore, which served as a hammer, the ribbon was hammered off into strips, which were afterward rudely fashioned, by means of two stones — one a hammer, the other an anvil — into knives, spearheads, arrow-points, fish-hooks, needles, and other utensils. The relics of the ancient copper miners are found in all parts of America, and some of the richest mines in the world are located upon the sites of prehistoric mines.

Copper is a tough, malleable metal of a reddish color which tarnishes quickly in air containing moisture and carbon dioxide. In the native state it sometimes occurs in regular octahedral crystals, which are also obtainable by the electric current. Copper forms two series of salts and no acids.

Sug. Examine the copper plates of a gravity battery which has been in operation several weeks.

Exercise. Write an essay, giving the uses of copper and describing the process of electrotyping.

The best solvent for copper is nitric acid, and a solution of the salt thus obtained is a good one for practice. Copper sulphate solution answers the same purpose.

THE PRINCIPAL COMPOUNDS OF COPPER ARE: —

(*a*) *Copper Sulphate*, or *Blue Vitriol*, $CuSO_4 + 5\ H_2O$; this salt is used in electrotyping, in calico printing, in the preparation of Paris green, and for galvanic batteries. How is it prepared?

(*b*) *Copper Nitrate*, $Cu(NO_3)_2$, which is used in calico printing. How is it prepared?

(*c*) *Cupric Sulphide*, CuS, and *Cuprous Sulphide*, Cu_2S, which are the *group-reagent precipitates*. These are obtained by passing hydrogen sulphide through the solutions of the corresponding copper salts.

(*d*) The principal *Oxides* of copper, *Cuprous Oxide*, Cu_2O, and *Cupric Oxide*, CuO. The former is used to impart a red color to glass; it occurs native. Cupric oxide is used in coloring glass green in imitation of the emerald. This oxide also occurs native as *Melaconite*. Both oxides may be prepared artificially. (See R. and S., Vol. II., Pt. I., pp. 329 and 330.)

GENERAL NOTE. The copper salts act as poisons when taken internally.

271. Tests for Copper. — 1. Any compound of copper may be reduced on charcoal, by the usual method, to minute red metallic beads.

2. Solutions are tested thus: (*a*) Make a borax bead upon a platinum wire; moisten with the solution and heat in the oxidizing-flame. If copper be present, the bead will be *green* while hot, *blue* when cold. (*b*) To the solution add: —

(1) An excess of ammonia, a blue solution;

(2) H_2S, a black precipitate.

3. Potassium ferrocyanide, K_4FeCy_6, in dilute solutions gives a reddish-brown solution; in concentrated solutions, a precipitate, Cu_2FeCy_6, of the same color.

4. Copper chloride colors the Bunsen flame blue.

NOTE. The tests by the blow-pipe for copper are as unsatisfactory as those for tin; the reduction occurs, but the beads are of microscopical dimensions. If the fused mass be rubbed in a mortar spots of copper become visible when the flux and charcoal are removed by washing.

272. To separate and identify Bismuth and Copper. — If the substance is a solid, dissolve it in nitric acid; then add an excess of ammonia. Bismuth hydroxide, $Bi(OH)_3$, is obtained as a white, flocculent precipitate powder, while the copper remains in the *blue* solution as a cupro-ammonium salt. Filter out the precipitate, dissolve it in hydrochloric acid and expel the excess of acid; again add water, when bismuthyl chloride, $BiOCl$, is precipitated as a white powder. This identifies the bismuth; the ***blue solution*** identifies the copper.

CADMIUM.

SYMBOL, Cd''. — ATOMIC WEIGHT, 112. — SPECIFIC HEAT, 0.0567. — MELTING-POINT, 315°.

273. **Occurrence.** — Cadmium is a somewhat rare metal, which is found in nature associated with zinc. Its sulphide, CdS, or Greenockite, also occurs in small quantities.

274. **Preparation.** — In smelting zinc, the cadmium is oxidized to form the compound CdO, which readily passes off in dark-yellow vapors. These vapors are condensed in suitable chambers, and afterward reduced to a metallic condition by heating in closed tubes with charcoal. The impure metal thus obtained is purified in the wet way, as in: —

EXP. 162 P. Dissolve a bit of cadmium in hydrochloric acid. After expelling any excess of acid, suspend a strip of zinc in the solution. The cadmium is precipitated as a spongy, gray precipitate. Collect, fuse to a bead, then oxidize strongly. What occurs?

275. **Properties, Uses, and Compounds of Cadmium.** — Cadmium was discovered in 1817 by Stromeyer in zinc carbonate from Salzgitter. It is a tin-white metal, which vaporizes at 860°. It oxidizes slowly in the air, and the surface of the metal is apt to present a yellowish tint, owing to the formation of the oxide, CdO. It takes fire if vaporized in the air.

Cadmium closely resembles tin in its physical properties; but, unlike tin, it has but few uses in the arts. Cadmium amalgam is used in filling teeth, since it is pasty at first, but afterwards hardens.

The best solvent for Cadmium is nitric acid. In hydrochloric acid and sulphuric acid it dissolves less readily. Employ the nitrate or the chloride as a working solution.

THE PRINCIPAL COMPOUNDS OF CADMIUM ARE: —

(*a*) *Cadmium Oxide*, CdO. How is this compound formed?

(*b*) *Cadmium Iodide*, CdI_2, which is used in photography; it is prepared by boiling metallic cadmium and iodine in water.

(*c*) *Cadmium Sulphate*, $3\ CdSO_4 + 8\ H_2O$, used in medicine in diseases of the eye.

(*d*) *Cadmium Sulphide*, CdS, used as a yellow pigment. It occurs native, as *Greenockite*, and is the *group-reagent precipitate* thrown down by hydrogen sulphide in acid solutions.

276. Tests for Cadmium. — 1. A solid heated on charcoal in the oxidizing-flame gives brownish-yellow fumes of CdO, also a coating of the same on the charcoal, if cadmium be present in sufficient quantity.

2. An acidulated cadmium solution with hydrogen sulphide gives a *yellow* precipitate insoluble in yellow ammonium sulphide.

3. A cadmium salt colors the borax bead *yellow* while hot, *colorless* when cold.

277. To separate and identify Bismuth, Copper, and Cadmium. — 1. To the solution containing salts of these three metals add ammonia in excess. The bismuth is precipitated, and identified as in Art. 272. The copper and cadmium remain in solution. The copper is identified by the blue solution.

2. Separate the copper and cadmium remaining in

solution thus: precipitate these two metals by hydrogen sulphide; filter out and wash the precipitate, then add hot dilute sulphuric acid to the precipitate on the filter-paper; the copper sulphide is unaltered, while the cadmium sulphide is dissolved and runs through, thus effecting the separation. Or, to the ammoniacal solution containing copper and cadmium add potassium cyanide until the blue color is destroyed; then pass hydrogen sulphide into it, and the cadmium is precipitated as the yellow sulphide, CdS, to be further identified by Art. 276.

NOTE. Copper sulphide is soluble in potassium cyanide, forming the double cyanide $6\,KCy.Cu_2Cy$. Cadmium forms a similar cyanide, but it is decomposed by hydrogen sulphide.

278. To separate and identify the Metals of the Second Group. — Acidulate the solution containing the salts of one or all of these metals with hydrochloric acid, and precipitate by hydrogen sulphide. The precipitate may be a sulphide of arsenic, antimony, tin, bismuth, copper, or cadmium; or sulphides of them all.[1]

Wash the precipitate, and wash it through into an evaporating dish; add yellow ammonium sulphide, and digest for some time, when the sulphides of division A dissolve, while the sulphides of division B remain unaltered. Filter and treat the filtrate as in 1, the remaining precipitate as in 2.

1. Add hydrochloric acid to the filtrate. This decomposes the compounds present, and precipitates the sulphides of tin, arsenic, and antimony. Filter out and wash the precipitate, and proceed according to Art. 263.

2. Dissolve the precipitate while on the filter-paper in hot nitric acid, and expel the excess of acid by evaporat-

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[1] Sulphides of lead and mercury may also be present.

ing the solution to dryness. Dissolve in water, and proceed by Art. 277, for bismuth, copper, and cadmium. (See Note 2.)

Note 1. Should the precipitate fail to dissolve completely in HNO_3, the residue is probably mercury, which was present in the original solution as mercuric salts. Therefore dissolve this residue in nitro-hydrochloric acid, and test by adding $SnCl_2$. (See Art. 246.)

Note 2. Before trying for bismuth, copper, and cadmium, be sure there is no lead salt in the solution. It is best to try a small portion of the solution with H_2SO_4 for lead; should a precipitate occur, add H_2SO_4 to the whole, which will remove the lead as a precipitate. Filter, and proceed with the solution by 277.

279. Separation of the Metals of Groups I. and II. — To a cold solution containing one or more metals of both groups add hydrochloric acid; the first group is precipitated, but not completely. (See Notes 1 and 2, Art. 278.)

280. Reactions in Group II. — Balance the following equations, and ascertain what operations they indicate, and what principles they illustrate: —

(1) $As + Cl + H_2O = H_3AsO_4 + HCl.$
(2) $As_2O_3 + HCl = AsCl_3 + H_2O,$
and $AsCl_3 + H_2O = H_3AsO_3 + HCl.$
(3) $Sb + Cl = SbCl_3.$
(4) $Sn + HCl = SnCl_2 + H.$
(5) $Bi + HNO_3 = Bi(NO_3)_3 + NO_2 + H_2O.$
(6) $Cu + HNO_3 = Cu(NO_3)_2 + NO + H_2O.$
(7) $Cd + HNO_3 = Cd(NO_3)_2 + NO + H_2O.$
(8) $H_3AsO_4 + H_2S = \underline{As_2S_3} + H_2O + S_2.$
(9) $SbCl_3 + H_2S = \underline{Sb_2S_3} + HCl.$
(10) $SnCl_2 + H_2S = \underline{SnS} + HCl.$
(11) $Bi(NO_3)_3 + H_2S = \underline{Bi_2S_3} + HNO_3.$
(12) $Cu(NO_3)_2 + H_2S = \underline{CuS} + HNO_3.$
(13) $Cd(NO_3)_2 + H_2S = \underline{CdS} + HNO_3.$

(14) $As_2S_5 + Cl + H_2O = H_3AsO_4 + HCl$
(15) $Sb_2S_5 + Cl + H_2O = H_4Sb_2O_7 + HCl$
(16) $SnS + Cl = SnCl_4 + S.$
(17) $H_3AsO_4 + H = AsH_3 + H_2O.$
(18) $AsH_3 + AgNO_3 + H_2O = H_3AsO_3 + \underline{Ag} + HNO_3.$
(19) $H_4Sb_2O_7 + H = SbH_3 + H_2O.$
(20) $SbH_3 + AgNO_3 = \underline{Ag_3Sb} + HNO_3.$
(21) $SnCl_2 + Zn = \underline{Sn} + ZnCl_2.$
(22) $PbS + HNO_3 = Pb(NO_3)_2 + S + NO + H_2O.$
(23) $Pb(NO_3)_2 + H_2SO_4 = \underline{PbSO_4} + HNO_3.$
(24) $Bi_2S_3 + HNO_3 = Bi(NO_3)_3 + S + NO + H_2O.$
(25) $Bi(NO_3)_3 + NH_4HO = \underline{Bi(OH)_3} + NH_4NO_3.$
(26) $Bi(OH)_3 + HCl = BiCl_3 + H_2O.$
(27) $BiCl_3 + H_2O = \underline{BiOCl} + HCl.$
(28) $CuS + HNO_3 = Cu(NO_3)_2 + S + NO + H_2O.$
(29) $Cu(NO_3)_2 + NH_4HO = Cu(NH_3)_2O, NH_4NO_3 + H_2O.$
(30) $CdS + HNO_3 = Cd(NO_3)_2 + S + NO + H_2O.$
(31) $Cd(NO_3)_2 + H_2S = \underline{CdS} + HNO_3.$
(32) $Sn + HNO_3 = \underline{SnO_2} + H_2O + NO.$
(33) $Sn + HNO_3 = Sn(NO_3)_2 + H_2O + NH_4NO_3.$
(34) $Sb + HNO_3 = \underline{Sb_2O_3} + H_2O + NO.$
(35) $Sb + HNO_3 = \underline{SbO_2} + H_2O + NO.$

QUERIES. Which equations show the precipitation of Group II. Which show special reactions or tests ?

THE RARE METALS OF GROUP II.

GOLD.

Symbol, Au'''. — Atomic Weight, 196.5.

281. Gold always occurs native owing to its feeble chemical affinity; it has been known since the earliest times, therefore, and ever highly prized. It occurs very widely distributed in the older sedimentary and igneous rocks, and rivers running through these rocks wash down fine particles of gold and sand. From these sands the miner separates the precious metal by washing in a shallow pan or cradle. Nuggets of gold of great value have been found in the various gold-bearing districts, especially in Australia. The largest deposits of gold are in the western United States and Australia.

Gold-mining by hydraulic power has been conducted on an enormous scale in the West. The auriferous deposits are loosened by powerful streams of water which are directed against them. Thus the detritus is loosened, and afterward carried down the mountain slopes in sluices in which are placed pockets containing mercury. The fine particles of gold are caught in the pockets, as they readily form an amalgam with mercury.

In quartz-mining, the coarse rocks are crushed by machinery, and the gold likewise extracted by amalgamation.

Gold may be obtained in a pure state by first dissolving any of its alloys in nitro-hydrochloric acid, when its principal salt, $AuCl_3$, is formed, and by then adding ferrous sulphate, $FeSO_4$, thus: —

$$2\,AuCl_3 + 6\,FeSO_4 = 2\,Au + 2\,Fe_2(SO_4)_3 + Fe_2Cl_6.$$

The finely divided gold thus obtained may be fused to a yellow bead on charcoal.

The uses of gold are many, but in a pure state it is too soft to wear well, hence it is alloyed with silver and copper. Gold is very malleable and ductile, and does not tarnish in the air. Its salts are few and of little interest to the beginner. Name the uses of gold.

The test for gold is the formation of the purple of Cassius, thus: —

Dissolve the substance in aqua-regia, and expel the excess of acid. Fill a test-tube half full of water, then add *one drop* each of stannous chloride, $SnCl_2$, and stannic chloride, $SnCl_4$; then add a few drops of the solution first made. If gold be present, a *purple* tint appears; but should the reagents be in excess, metallic gold is reduced, and the color is brownish or reddish-black.

NOTE. A gold electroplating solution is made by adding potassium cyanide to gold chloride.

PLATINUM.

SYMBOL, Pt''''.—ATOMIC WEIGHT, 195.

282. Platinum is a silver-white, lustrous metal of great value to the chemist; without it, many chemical processes would be impossible, and our knowledge of the rare elements would be less extended.

It was probably discovered about three hundred years ago, but its properties and preparation have not been understood for more than one century.

It occurs only native, and always together with several kindred metals; it occurs in many localities, but in small quantities.

Platinum is obtained from its ores by first dissolving them in aqua regia, when platinic chloride, $PtCl_4$, is formed, together with the chlorides of the accompanying metals; ammonium chloride is then added, when a double chloride of platinum and ammonium is precipitated, viz., $(NH_4)_2PtCl_6$. This precipitate when heated yields spongy platinum, which is afterwards fused in lime crucibles by means of the oxy-hydrogen blow-pipe.

The high melting-point of platinum and its power of resisting the action of solvents, together with its malleability and ductility, render it most useful in chemical laboratories, where it is used as wire, foil, battery-plates, crucibles, weights, etc. Platinum may be welded like iron. It possesses a remarkable property of condensing gases upon its surface, especially when in a spongy state, as exhibited when a stream of hydrogen gas is directed against it; the hydrogen is thus ignited. Platinum wire acts similarly, and may even decompose a gas, as shown when a heated spiral is held in the fumes of ammonia or ether: the wire continues to glow, so great is the action upon its surface.

The salts of platinum are very numerous, but as they are used very little, they need not be considered here.

Nitro-hydrochloric acid is the best solvent for this metal.

The test for platinum is made thus: —

Dissolve the substance in aqua regia, expel any excess of acid, add NH_4Cl, when a yellow crystalline precipitate is thrown down, thus: —

$$PtCl_4 + 2\,NH_4Cl = (NH_4)_2PtCl_6.$$

Spongy platinum is to be had from this precipitate upon heating strongly.

General Note. Do not fuse any of the salts of the easily reducible metals on platinum, since they form fusible alloys with it, as will the silicon in charcoal, when platinum is heated in contact with the glowing coals. Do not heat a platinum crucible in a smoky flame, which will cause it to blister.

Try the purity of platinum by boiling in HCl, then in pure HNO_3. It should not dissolve.

To clean a platinum crucible, fuse acid potassium sulphate, $KHSO_4$, in it.

PALLADIUM.

Symbol, Pd''. — Atomic Weight, 106.

283. Palladium, a silver-white metal resembling platinum, occurs in connection with gold and platinum ores. It was first prepared by Wollaston, in 1804. Its uses in the arts are few, the chief ones being to make graduated scales for astronomical instruments, to plate silverware, and to take the place of gold in dentistry. Its best solvent is nitric acid, but spongy palladium is readily soluble in hydrochloric acid. The nitrate and chloride of palladium are used to separate chlorine, bromine, and iodine; but these reagents are too expensive for general use.

Palladium is detected by adding potassium cyanide to its solution in hydrochloric acid. A yellowish-white precipitate, soluble in hydrochloric acid and ammonia, is thrown down. It also gives a black precipitate with potassium iodide insoluble in hydrochloric acid.

RUTHENIUM.

SYMBOL, RU''. — ATOMIC WEIGHT, 103.5.

284. Ruthenium also resembles platinum. It was discovered, in 1845, by Claus, in the Ural platinum ores. It is very little used in the arts, nor are its salts particularly valuable.

Ruthenium is detected by passing hydrogen sulphide through its solution: the solution turns blue, afterwards brown. Also, when water is added to its chlorides, an inky, soluble oxychloride is formed.

IRIDIUM.

SYMBOL, IR''. — ATOMIC WEIGHT, 193.

285. Iridium occurs, as the preceding metals, in small grains, alloyed with platinum or osmium. It forms a valuable alloy with platinum, consisting of 1 part iridium and 9 parts platinum, which is very hard, elastic, insoluble, and unchanging in the air; it also takes a splendid polish and has a small coefficient of expansion, hence its use in making the standard measure of the metric system. Iridium alloys dissolve in aqua regia.

Iridium is very refractory; but it may be fused (as a phosphide) at a high temperature by the addition of phosphorus. The phosphide is adapted to many purposes where hardness and the property of resisting chemical action are requisite. The phosphorus can be withdrawn, however, by repeatedly heating the phosphide in contact with lime. Iridium or the compounds mentioned are used for the tips of gold pens, for "stylographic pens," and sometimes for the bearings of chemical balances. For valuable information concerning Iridium see *The Chemical News* for Jan. 1, 1885, p. 1, and Jan. 9, 1885, p. 19.

Iridium is detected by the dark-red crystalline precipitate formed by adding ammonium chloride to its concentrated solutions.

RHODIUM.

SYMBOL, Rh''. — ATOMIC WEIGHT, 104.

286. Rhodium also occurs with platinum, and was discovered in 1804 by Wollaston. It remains in solution after precipitating the platinum with ammonium chloride, and is to be obtained from this liquor. It is but slightly soluble in any solvent, but its alloys are soluble in aqua regia, when the proportion of rhodium is very small.

Rhodium is reduced from acid solutions by metallic zinc.

OSMIUM.

SYMBOL, Os''. — ATOMIC WEIGHT, 199.

287. Osmium likewise occurs with platinum, and is remarkable as forming a volatile oxide, OsO_4. This metal is the heaviest substance known, its specific gravity being 22.477. It has never been fused. An alloy of osmium and iridium is used to tip gold pens; also to make the bearings of mariner's compasses.

Osmium is detected by the odor of its volatile compound, OsO_4, obtained by treating its soluble compounds with nitric acid.

TUNGSTEN.

SYMBOL, W^{iv}. — ATOMIC WEIGHT, 184.

288. Tungsten occurs most plentifully in Wolfram, a tungstate of iron and manganese, and has not been prepared in a coherent state. Its proposed industrial use is to improve tool steel.

Tungsten is detected by first fusing any of its compounds with potassium hydroxide, and afterwards dissolving the fused mass in hydrochloric acid; into this solution a strip of zinc is immersed; the solution turns blue if tungsten be present.

MOLYBDENUM.

SYMBOL, Mo''. — ATOMIC WEIGHT, 96.

289. Molybdenum is a silver-white metal, occurring in Molybdenite, MoS_2; this sulphide was mistaken, in ancient times, for plumbago, which substance it closely resembles. Ammonium molybdate is an important test for phosphoric acid (see App.). Ammonium phospho-molybdate, $2\,(NH_4)_3PO_4 + 22\,MoO_3 + 12\,H_2O$, is used in chemistry as a reagent for detecting alkaloids.

Molybdenum is detected in the same way as tungsten, the solution turning successively blue, green, and brown.

EXERCISES.

1. Dissolve in nitric acid a small silver coin, and see what metals you can detect in the solution.

2. Allow a drop of molten bismuth to fall upon the floor, and note what occurs.

3. What metals have atomic weights of about 104? About 195? Find their positions in the table on p. 221. By what similarity of properties are they marked?

4. How can you show by the same table that iron, cobalt, nickel, chromium, manganese, and copper are closely related?

5. What elements are closely related to phosphorus?

6. Dissolve a bit of worn-out "gold" jewelry in aqua regia and determine what metals are present.

7. Compute the atomic heat and the atomic volume of the common metals of the second group.

8. Analyze a sample of "antimony black" obtained from the drug store.

"Pulverized Sb_2S_3 is known as 'antimony black' although a mixture of anthracite and marble is sometimes sold under that name." — WARDER.

CHAPTER XVII.

THE THIRD GROUP METALS.

290. The metallic hydroxides and sulphides of this group are soluble in dilute acids, but insoluble in alkaline solutions. There are different methods of separating this group from the other groups; and, moreover, the individual metals of the third group may be separated and identified by different processes. We shall here pursue that plan which is as simple as possible, and which is in most cases preferable. Just as in the preceding group, we may likewise divide the commonly occurring metals of this group into two classes. We may obtain the precipitates of this group as follows: Suppose the solution contains any or all the metallic salts of the five groups. The first and second group metals are removed by hydrochloric acid and hydrogen sulphide; in any chromium compound that may be present chromium is now combined as a base through the agency of the reagents employed, while iron salts by the same means are reduced to the ferrous condition. In case no first and second group metals are present, it is still necessary to use hydrochloric acid and hydrogen sulphide to insure that chromium may be present as a base (Art. 303, 4, Note). The solution is now boiled to expel any excess of hydrogen sulphide; then nitric acid is added and the whole boiled a moment to oxidize iron salts to the ferric condition; the solution is now ready for the application of the group reagents.

Ammonia and ammonium chloride are immediately added; thus the hydroxides $Fe_2(OH)_6$, $Cr_2(OH)_6$, and $Al_2(OH)_6$ are precipitated. This precipitate is now removed by filtering. To the filtrate ammonium sulphide, $(NH_4)_2S$, is added; this gives the precipitates NiS, CoS, MnS, ZnS. Let us indicate these divisions as in the previous group: —

Division	Metals
DIVISION A	Iron. Chromium. Aluminum.
DIVISION B	Nickel. Cobalt. Manganese. Zinc.

SUG. Try to determine why it is necessary to oxidize ferrous to ferric salts, and why chromium, if present, must be a base.

The most strongly marked characteristics of the metals of this group are as follows: —

(*a*) Their surfaces gradually oxidize in the air, forming oxides most of which are to be reduced to the metallic state only at a white heat in the presence of reducing agents.

(*b*) On charcoal many of these metals cannot be readily reduced from their compounds by means of the blow-pipe.

(*c*) Their oxides and hydroxides are insoluble in water; in certain cases, however, the hydroxides are soluble in an excess of the alkali used as a precipitant.

(*d*) None of the common metals of this group give spectra or color the flame unless the temperature be higher than that of the Bunsen flame.

(*e*) Most of these metals give a characteristic color to the borax or microcosmic bead, when heated on a platinum loop before the blow-pipe.

GENERAL NOTE. Most of the common metals of the third group and those of the fourth and fifth cannot be reduced to the metallic state by any means likely to be at the command of workers in small laboratories. On this account, and by reason of the fact that the general principles underlying the reduction of the metals have been illustrated previously, the attention of the student may now most profitably be given to the analytical reactions of the various metallic salts. In case time permits, it would also be well to encourage the student to prepare such of the salts as the apparatus, chemicals, etc., at his command will permit. Owing to his previous training, the student will now be able, in his work, to devise methods and to keep his notes accurately and intelligently. In furtherance of this object many topics, by aid of the descriptions given, may be rewritten by him in the form of experiments. Let him also make tables for each metal showing the effect of precipitants and solvents upon the salts of that metal.

IRON.

SYMBOL, FE''. — ATOMIC WEIGHT, 56. — SPECIFIC HEAT, 0.1140. — MELTING-POINT, A WHITE HEAT.

291. Occurrence. — Native metallic iron occurs in insignificant quantities, and as meteoric iron; it is also said to fall everywhere and constantly upon the earth as a fine dust. Meteorites frequently contain iron; the largest mass on record weighs 32,000 pounds, while others of less weight are frequently found.

The iron compounds are present in most rocks and soils, and play an important part in the animal and the vegetable economy; the color of the blood and of all vegetation is due to the presence of iron.

The ores of iron, from which the metal is reduced, usually occur in somewhat limited areas, but in many localities. In the United States, the Lake Superior region supplies very valuable ores; the Southern, Eastern, and Western States likewise produce immense quantities. In the Old World, Scandinavia, Elba, Great Britain, the Ural Mountains, and some other parts of Europe are famous iron-producing regions.

Among the many ores of iron, space permits a description of only those varieties which are valuable to commerce.

1. *Hæmatite*, or *Specular Ore*, Fe_2O_3, occurs in veins, beds, and pockets. This ore is frequently of great purity, and is the ore chiefly employed in the reducing furnaces of the United States.

It assumes different modifications, as: —

(*a*) *Amorphous Ore*, a reddish, massive variety which resembles, in appearance, "iron rust."

(*b*) *Micaceous Ore*, occurring in glittering scales.

(*c*) *Granular Ore*, of a crystalline structure.

(*d*) *Grape Ore*, occurring in masses resembling bunches of grapes, and therefore frequently called *botryoidal ore.*

2. *Brown Hæmatite*, $Fe_2O_3 + Fe_2(OH)_6$, is frequently known as *bog ore*, and is the ore chiefly employed for reduction in France and Germany.

3. *Magnetite*, or *Lodestone*, Fe_3O_4, is the well-known natural magnet; it occurs in all the previously mentioned localities. A good quality of iron is obtained from this ore, but its reduction is somewhat difficult.

4. *Siderite*, or *Spathic Ore*, is a carbonate of iron, $FeCO_3$, containing also the carbonates of calcium, magnesium, and manganese. The renowned Styrian steel is manufactured from this ore at Erzberg.

5. *Argillaceous Ore*, or *Clay Iron-Stone*, occurs in connection with coal, and is the ore chiefly employed in England. This ore also occurs in Maryland, Pennsylvania, and Ohio.

292. Preparation of Iron. — The reduction of iron as now carried on is one of the greatest industries of the age. In the primitive stages of this industry the process was a simple one which, however, permitted the employment of the purest ores only.

A simple hearth was built with an opening at the bottom to admit a blast of air from a rude bellows, while another opening allowed the exit of the slag. After heating the hearth, the ore and fuel were arranged in layers, and a continuous blast was maintained. In from four to six hours a porous "bloom" of iron weighing from 5 to 30 lbs. was obtained. This "bloom" was then brought into the requisite shape by alternately heating and hammering it. Since the limits of our work prevent the giving of a consecutive history of the improvements on this method, it must suffice to say that the developments have been such that the present processes are applicable to any ore.

The process now employed consists of two steps: —

(*a*) The production of *cast iron* from the ore;

(*b*) The manufacture of *wrought* iron from cast iron.

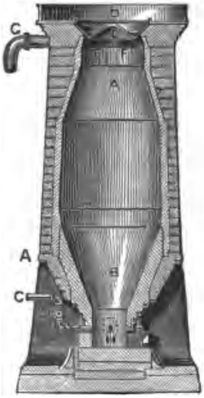

Fig. 19.

(*a*) The ore is first crushed and then mixed with crushed limestone and coal, when it is ready for the furnace.

The best form of blast-furnace is shown in Fig. 19. This furnace, which is from 50 to 90 feet high, and from 14 to 20 feet broad in its widest part, is constructed of masonry and has a lining of fire-brick. The whole stack is enclosed down to the point A in riveted iron boiler-plates. The masonry of the stack does not extend below A before the furnace is prepared to go into blast, but strong iron pillars (not shown in the cut) extend from that point to the ground. The hearth H consists of fire clay. It is here that the molten metal collects. This hearth has two openings, the upper one for removing the slag, the lower one for drawing off the molten metal. The top of the stack D is funnel-shaped and is closed by an inverted cone, E, which lowers to admit the ore, fuel, etc., when the furnace is in operation, and which can be quickly raised again to close the opening.

When a furnace is about to go into blast, the spaces H and B are filled with cord-wood, after which the whole portion below A, excepting the egress openings for the molten metal and slag, is enclosed by masonry; a number of blow-pipes, or "Tuyeres," C, are also inserted, through which powerful blasts of air are to be driven.

The wood is now ignited, the blast is started, and coal is introduced through the funnel D. When the interior of the furnace is sufficiently heated, the ore, mixed with coal and limestone, is admitted through D at regular intervals.

Barring accidents, a furnace, after going into blast, runs night and day, shutting down but once or twice a year to renew the fire-brick linings and to make other needed repairs.

The chemical changes which take place in the stack are not thoroughly understood, but the products obtained are cast iron, a glassy slag, carbon dioxide gas, carbon monoxide gas, hydrogen, and perhaps certain hydro-carbons, graphite, and cyanogen. The gases are not wasted, but are led through the pipe G — whose opening is seen at F — into burners situated under the boilers which supply steam to the engines used to drive the crushers, hoisters, air-condensers, etc., etc.

The cast iron of the blast-furnace is not pure iron, but contains carbon and silicon, with traces of phosphorus, arsenic, and sulphur, besides other metals in small quantities.

(*b*) The *second step* is changing the cast iron into wrought iron. This is accomplished by the processes termed "refining" and "puddling," which consist in burning out the impurities and hammering the metal into coherence. The metal is then rolled into bars and sent to market.

Another important branch of the iron industry is the manufacture of steel.

Steel, in its chemical composition, stands midway between cast and wrought iron in the amount of carbon and silicon which it contains. It was formerly prepared at great expense by heating wrought iron in contact with carbon. The Bessemer process, however, has cheapened the production of steel, so that its use is becoming general.

This process is, briefly, as follows: —

Cast iron is melted in a cupola furnace and run into an egg-shaped vessel called a "converter," which is so arranged that a blast of air may be driven up through the molten iron.

In this way the carbon and silicon of the cast iron are burned out; then a sufficient quantity of pure molten cast iron is added to convert the whole into steel. In about half an hour from five to twelve tons of steel are thus obtained from one converter.

293. Properties, Uses, and Salts of Iron. — Pure iron is a nearly silver-white metal, which rusts easily when exposed to dampness, ferric hydroxide and oxide being formed upon its surface. Iron is a very tenacious metal, and possesses the peculiar property of softening before it melts, thus allowing different pieces to be "welded."

The uses of iron and steel are so numerous and various that this age has well been termed the IRON AGE.

EXERCISES. Name the uses of cast iron; wrought iron; steel. What is meant by the "temper" of steel? How is steel tempered? How is cast iron *chilled?* What is malleable iron? How are twist gun-barrels made? Laminated steel gun-barrels? Damascus steel gun-barrels? (Ask your gunsmith about the value and manufacture of gun-barrels.) How do cast iron, wrought iron, and steel differ in their properties? Can you "clinch" a common cut iron nail? Try it. Heat it red hot, cool it slowly, and then try. How can you draw the temper of a steel tool? State the effects of magnets upon iron and steel. In what acids will iron dissolve? Which acid is the best solvent? (Try, at least, H_2SO_4, HNO_3, HCl, and aqua regia.) What differences are there between the composition of cast iron, of wrought iron, and of steel?

Iron, like mercury (which see), forms two series of salts. Its compounds are numerous and important. Only a few of the most important ones can be given here.

THE PRINCIPAL COMPOUNDS OF IRON ARE: —

(*a*) *The Oxides*, FeO, Fe_2O_3, and Fe_3O_4. The last two, which are ores of iron, have already been noticed. *Ferric Hydroxide*, $Fe_2(OH)_6$, is a brownish precipitate obtained by adding ammonia to a cold solution of ferric chloride, Fe_2Cl_6; this hydroxide is used in medicine. It is the *group-reagent precipitate*. The first oxide, FeO, is unimportant.

(*b*) *Ferric Chloride*, Fe_2Cl_6. This salt is prepared by dissolving iron wire in hydrochloric acid, after which the solution is thoroughly saturated with chlorine gas. It is used in medicine; in the laboratory it is employed as a reagent.

Ferrous Chloride, $FeCl_2$, is prepared by dissolving iron wire in hydrochloric acid; it is also used in medicine.

(*c*) *Ferrous Sulphate*, *Green Vitriol* or *Copperas*, $FeSO_4 + 7\,H_2O$. This salt is obtained when iron or ferrous sulphide is dissolved in sulphuric acid. It is used as a reagent and for preparing inks, dyes, and Prussian blue. Its uses as a deodorant and a disinfectant have already been mentioned.

(*d*) *Ferrous Sulphide*, FeS. This useful compound is made by stirring a portion of molten sulphur with a white-hot rod of wrought iron until the sulphur disappears. It is used in the laboratory for obtaining hydrogen sulphide.

(*e*) *Iron Pyrites*, or *Fool's Gold*, FeS_2, occurs native as yellow, shining cubical crystals. It is found in various geological formations. Its principal use is for manufacturing sulphuric acid.

Fe_2S_3 probably occurs in magnetic pyrites. It can be produced artificially, but is of small importance.

(*f*) *Potassium Ferrocyanide*, or *Yellow Prussiate of Potash*, K_4FeCy_6. This salt is obtained by heating scrap iron in closed iron retorts with potash and animal matter such as hoofs, horns, hides, feathers, etc.

This salt is of great importance, since it serves as the point of departure in the preparation of all the cyanogen compounds. In the laboratory it is used as a reagent for detecting iron. In the arts it is used for preparing Prussian blue, $(Fe_2)_2(FeCy_6)_3$ or Fe_7Cy_{18}. This pigment is obtained when ferrous sulphate or ferric chloride is added to the ferrocyanide, K_4FeCy_6.

(*g*) *Potassium Ferri-cyanide*, or *Red Prussiate of Potash*, K_3FeCy_6, is obtained by oxidizing K_4FeCy_6 by the action of chlorine. It is used to some extent as a reagent in the laboratory.

294. Tests for Iron. — 1. It is best to dissolve solids, and to test by 2. The blow-pipe tests are not satisfactory to beginners.

2. Any solution is tested for iron by the reagents, potassium sulpho-cyanide, KCyS, and the ferro and ferricyanides, K_4FeCy_6 and K_3FeCy_6. The change produced upon any solution depends upon whether the substance under examination contains a ferrous or a ferric salt. These changes are exhibited by the following table: —

Reagent.	Ferric Salt.	Ferrous Salt.
KCyS	Red sol. $[Fe_2(CyS)_6]$	No change.
K_4FeCy_6	Deep blue prec. $[Fe_4(FeCy_6)_3]$	Pale blue prec. $[K_2Fe(FeCy_6)]$
K_3FeCy_6	No prec. Reddish brown sol.[1]	Deep blue prec. $[Fe_3(FeCy_6)_2]$

3. By employing a ferric salt (Fe_2Cl_6) and a ferrous salt ($FeSO_4$) as reagents, it is evident that the table given in 2 affords tests for *Ferrocyanic* and *Ferricyanic acids* or their derived salts.

EXERCISES.

1. Ignite in the Bunsen flame any ferrous salt, as $FeSO_4$, on platinum foil. Try the residue with a magnet. Is it magnetic? What oxide of iron is thus obtained?

2. Heat any ferric salt, as $Fe_2(NO_3)_6$, on charcoal in the reducing-flame. Do you obtain the same oxide as before?

3. Prepare, solid, Fe_2Cl_6, and test for ferric salts. *Write out a description of the process, etc., in the form of an experiment.*

4. In what experiment is the action of iron in the borax bead described? When have you prepared $FeSO_4$?

5. Try to precipitate a solution of $FeSO_4$ with NH_3 and NH_4Cl. Acidulate a fresh portion of the solution with HNO_3; boil, and try as before. Explain.

CHROMIUM.

Symbol, Cr'''.—Atomic Weight, 52.—Specific Heat, 0.09975.
—Melting-Point (higher than that of Platinum).

295. Occurrence.—Chromium is a somewhat rare metal which never occurs free in nature. Its chief ores are Crocoisite, or chrome yellow, $PbCrO_4$, and chrome ironstone, $Cr_2O_3(FeO)$. The color of many minerals is due to the presence of traces of the chromium compounds.

296. Preparation.—Chromium is not employed in the metallic state. It is obtained for scientific purposes by mixing its oxide with sugar, after which the mixture is strongly heated in a lime crucible. Thus obtained, it is a gray, crystalline powder.

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[1] If the color is very dark, dilute the solution until you can see whether a blue precipitate is not also formed. In such a case, you have both the ferric and ferrous salts present.

297. Properties, Uses, and Compounds of Chromium. — Metallic chromium presents a crystalline, silvery appearance under the microscope. Its principal use is to harden steel, to which it imparts a superior hardness.

The best working solutions for chromium are solutions of chromous chloride, $CrCl_2$; *chrome alum; potassium chromates; or the acid chromate.* Metallic chromium is soluble in hydrochloric acid, $CrCl_2$ being obtained.

THE PRINCIPAL CHROMIUM COMPOUNDS ARE: —

(*a*) *The Oxides*, Cr_2O_3 and CrO_3. Chromic oxide, Cr_2O_3, is used in coloring glass and enamel green. It is obtained by fusing potassium bichromate, $K_2Cr_2O_7$, with sulphur or with ammonium chloride, after which the fused mass is treated with water. The oxide CrO_3 may be regarded as the anhydride of the hypothetical chromic acid, H_2CrO_4: $H_2O + CrO_3 = H_2CrO_4$.

Chromic Hydroxide, $Cr_2(OH)_6$, is the *group-reagent precipitate* obtained by adding ammonia and ammonium chloride to the solution of a salt in which chromium is combined *as a base.*

Guignet's Green, $Cr_2O(OH)_4$, is now largely used as a pigment; it is sold in drug stores under the name *chrome green.* This pigment is prepared by fusing potassium bichromate mixed with crystallized boric acid in quantities proportional to the molecular weights of the substances employed. The fused mass is then ground to a fine powder.

(*b*) *Potassium Chromium Sulphate*, or *Chrome Alum*, $K_2Cr_2(SO_4)_4 + 24\,H_2O$. This salt is obtained as a by-product in the manufacture of alizarine and in many other oxidations. It is used in dyeing, tanning, and in calico printing.

(*c*) *Potassium Chromate*, K_2CrO_4. This salt is obtained by adding potassium hydroxide to a solution of potassium bichromate. It is used in the laboratory as a reagent.

(*d*) *Potassium Bichromate*, $K_2Cr_2O_7$, or *Acid Potassium Chromate*. This is an important salt obtained from chrome iron ore by three steps: (1) Roasting the ore to oxidize it; (2) fusing the roasted ore with lime and potassium carbonate; (3) lixivating the fused mass with as little water as possible, and then treating the liquor with sulphuric acid. This salt is used to prepare chrome yellow, $PbCrO_4$, to dye wool, and to prepare other chromium compounds. It is also used in the autotype process and as a reagent.

The relation between potassium chromate and bichromate may be understood best by considering the acids from which they are derived. Hypothetical chromic acid probably has the composition H_2CrO_4. Its normal potassium salt is K_2CrO_4. If we imagine chromic acid to lose water according to this equation,—

$$2\,H_2CrO_4 - H_2O = H_2Cr_2O_7,$$

we have left the acid from which potassium bichromate, $K_2Cr_2O_7$, is derived, bichromic or pyrochromic acid.

QUERY. Are there any similar relations met with in connection with sulphur compounds? Compare carefully sulphuric and chromic acids.

(*e*) *Lead Chromate*, or *Chrome Yellow*, $PbCrO_4$. This compound occurs in nature as crocoisite, and is also prepared artificially by precipitating a lead salt with potassium bichromate; used in calico printing and as a pigment. *Chrome Red*, Pb_2CrO_5, and *Chrome Orange*, a mixture of chrome red and chrome yellow, are much used as paints.

The following peculiarities will be noticed concerning the chromium compounds: As a base it forms the chromous and chromic salts, of which chromous chloride, $CrCl_2$, and chromic chloride, Cr_2Cl_6, may be taken as examples. As an acid-forming element, it gives rise to three series of salts, — the chromites, chromates, and the bichromates;

of these, ferrous chromite, $FeCr_2O_4$, lead chromate, $PbCrO_4$, and potassium bichromate, $K_2Cr_2O_7$, may be taken as representatives.

NOTE. As the chromates do not yield precipitates with NH_3 and NH_4Cl, it is advisable to use a salt like chrome alum, in which chromium is a base, for the solution which the beginner is to analyze for the third group metals. The use of HCl and H_2S may then be dispensed with.

298. Tests for Chromium. — 1. Chromium, free or in compounds, gives the borax or microcosmic bead an *emerald-green* color.

2. Fuse the substance to be tested on platinum foil or porcelain with KNO_3 and Na_2CO_3. These reagents will oxidize any chromium present to a chromate. Now dissolve the yellow mass in water, acidify with acetic acid, and add lead acetate; a dense yellow precipitate, $PbCrO_4$, indicates chromium.

3. A *chromate* or a *bichromate* may be recognized by adding: —

(*a*) H_2S, when the color changes to green.

(*b*) Lead acetate, which gives *yellow* lead chromate, $PbCrO_4$.

(*c*) Silver nitrate, which gives brownish-*red* silver chromate, Ag_2CrO_4.

NOTE. Potassium chromate is a yellow crystalline solid, while the bichromate is of a red color.

EXERCISES.

1. Prepare (and describe its preparation as an experiment) Cr_2O_3.
2. Similarly prepare and describe Guignet's green.
3. Likewise prepare and describe K_2CrO_4 and chrome yellow.
4. Try to precipitate a chromate with NH_3 and NH_4Cl. Acidulate with HCl a fresh portion of chromate, pass H_2S, and try the same precipitants. What results? Warm a chromate with $(NH_4)_2S$. What results?

ALUMINUM.

SYMBOL, AL'''. — ATOMIC WEIGHT, 27. — SPECIFIC HEAT, 0.2140. — MELTING-POINT, 700° C.

299. Occurrence. — Next to oxygen and silicon, aluminum is the most plentiful and widely-occurring element. It is the basis of all clayey soils, and occurs as feldspar or $K_2Al_2Si_6O_{16}$ in granite, gneiss, syenite, trachite, porphyry, etc.

Albite, a sodium feldspar, also occurs in large quantities. Kaolin, or porcelain clay and china clay, is feldspar which has been disintegrated and decomposed by exposure to the atmosphere.

The different varieties of garnet, mica, and slate stones are important silicates of aluminum and other metals. Alumina or aluminum oxide, Al_2O_3, is known as corundum or emery when coarse, but when crystallized it constitutes the important jewels sapphire, ruby, oriental emerald, oriental topaz, and oriental amethyst.

300. Preparation. — Metallic aluminum is prepared from bauxite, $Al_2Fe_2O_8H_4$.

From this substance the oxide of aluminum, Al_2O_3, is first prepared thus: The bauxite is heated with soda in a reverberatory furnace, when a soluble compound of sodium and aluminum is formed; this compound is dissolved in water, and a current of carbon dioxide passed through the solution, precipitating the required alumina.

This oxide is then mixed with charcoal and sodium chloride and heated to a white heat; then chlorine gas is passed through the mixture, thus forming a volatile double chloride of aluminum and sodium, from which the metal is obtained by fusing with metallic sodium and cryolite.

Aluminum (alloyed with copper) has lately been obtained directly from corundum, Al_2O_3, by reduction with carbon, in the absence of air, in an electric circuit.

301. Properties, Uses, and Salts of Aluminum. — Aluminum is a white, malleable metal which does not tarnish or oxidize under ordinary circumstances. Its extreme lightness (sp. grav. = 2.67), elasticity, tenacity, and the fact that it is not easily oxidized fit it for many uses which the cost of its production alone prevents. It is chiefly employed at present in making philosophical instruments. Aluminum forms valuable alloys with copper and silver.

The best solvent for aluminum is hydrochloric acid.

THE PRINCIPAL COMPOUNDS OF ALUMINUM NOT PREVIOUSLY MENTIONED ARE: —

(*a*) *Sodium Aluminate*, $Na_6Al_2O_6$(?), obtained by fusing bauxite with sodium sulphate and carbon; it is used as a mordant in dyeing and calico printing, for preparing colored lakes, and for sizing paper.

(*b*) *Aluminum Sulphate*, $Al_2(SO_4)_3$. This is used in immense quantities as a mordant and for weighting paper, and is obtained by roasting kaolin, which is then dissolved in sulphuric acid, and the solution evaporated till it will solidify when cool.

(*c*) *The Alums*, of which there are many. We give the formulae of the most important: $K_2Al_2(SO_4)_4 + 24\ H_2O$; $Ag_2Al_2(SO_4)_4 + 24\ H_2O$; and $(NH_4)_2Al_2(SO_4)_4 + 24\ H_2O$.

(*d*) *Aluminum Hydroxide*, $Al_2(OH)_6$, obtained by adding ammonia to a soluble salt of aluminum; it is the white, gelatinous *group-reagent precipitate.*

(*e*) *Phosphates of Aluminum.* The principal one is *turquois*, a well-known jewel, which owes its bluish or greenish color to the presence of copper. Its formula is $Al_2PO_4(OH)_3 + H_2O$; the ancient gem was cut from *odontolite*, a fossil tooth or bone.

(*f*) *Silicates of Aluminum.* The principal ones are: —

Topaz, $Al_2F_2SiO_4$. A yellowish-colored jewel whose coarser forms are frequently used instead of emery for polishing purposes.

Beryl, $Al_2Be_3Si_6O_{18}$. A green variety, the true *emerald*, is used in jewelry. What is the "oriental emerald?"

Lapis Lazuli, a bluish mineral of unknown chemical constitution containing silicates of aluminum and sodium, besides sulphur. It is used for ornamental purposes, and when powdered is known as *ultramarine*, a valuable paint. The best ultramarine is now manufactured in large quantities by fusing together a very fine variety of clay, sand, sulphur, and resin.

302. Tests for Aluminum. — 1. Solids are fused with Na_2CO_3 or $HKSO_4$ and then dissolved in hydrochloric acid. This solution is treated as in

2. Add an excess of NH_4Cl and ammonia to the solution. Aluminum gives a white, gelatinous precipitate, $Al_2(OH)_6$.

3. The solution may be tested further by adding to another portion: —

(*a*) Na_2CO_3, — the precipitate, $Al_2(OH)_6$;

(*b*) Na_2HPO_4, — a white precipitate, $Al_2(PO_4)_2$, soluble in KOH, insoluble in acetic acid.

EXERCISES.

1. Obtain at your druggist's different kinds of alum, and determine what bases are present.
2. For a valuable paper on alum as a purifier for drinking-water, see the "Chemical News," May 22, 1885, p. 241.
3. Does aluminum act both as a base and an acid-forming element?
4. Ask your jeweller to show you specimens of turquois, beryl, topaz, ruby, sapphire, emerald, and lapis lazuli. How do their values compare?
5. Examine baking powder for alum.

303. To separate and identify Iron, Chromium, and Aluminum. — From the solution remove the first and second group metals (if any be present) by means of HCl and H_2S. Boil the filtrate (if HCl and H_2S were employed) to expel all the hydrogen sulphide. If any iron salts be present, they are now in the ferrous condition; therefore add a little nitric acid, and boil a short time to oxidize the ferrous to ferric salts. The solution is now prepared for the following treatment: —

1. Add ammonia till the solution is alkaline, and then add ammonium chloride; the precipitate obtained may be any or all of the hydroxides, $Fe_2(OH)_6$, $Cr_2(OH)_6$, $Al_2(OH)_6$. Filter and wash the precipitate.

2. Pierce the point of the filter-paper, and wash the precipitate through into a beaker-glass; add potassium or sodium hydroxide, and boil for several minutes. The hydroxides of iron and chromium remain unchanged, while the aluminum is dissolved. Now filter the contents of the beaker, and treat the precipitate for iron and chromium as in 3 and 4. Treat the filtrate for aluminum as in 5.

3. Dissolve a portion of the precipitate in HCl, and test for iron as in 294, 2. If iron be present, test a portion of the original solution to determine if the salt be in the ferrous or ferric condition.

4. Fuse on platinum foil a second portion of the same precipitate with sodium carbonate and potassium nitrate Any chromium present is thus oxidized to a chromate. Dissolve the fused mass in water, and test by 298, 3. Test the original solution for chromates.

NOTE. If the original solution contained chromates, they would be reduced by H_2S to salts in which chromium would give a precipitate with NH_4Cl and NH_3. If no first and second group metals were present, and

HCl and H_2S were not employed, it would be necessary to test the original solution (unless it is colorless) directly for chromates, since chromates do not give $Cr_2(OH)_6$ with NH_3 and NH_4Cl. In case the solution contains the salts of the metals of division B or those of the fourth group, it is necessary to use HCl and H_2S.

5. To the filtrate from 2 add sufficient hydrochloric acid barely to acidify it; then add ammonia; a white precipitate, $Al_2(OH)_6$, identifies aluminum.

Sug. Explain the significance of these equations: —

(1) $2\ H_2CrO_4 + 6\ HCl + 3\ H_2S = Cr_2Cl_6 + 3\ S + 8\ H_2O.$
(2) $2\ Fe'' + 8\ \underset{\text{hot}}{HNO_3} = Fe'''_2(NO_3)_6 + 2\ NO + 4\ H_2O.$
(3) $Fe'''_2(NO_3)_6 + H_2S = 2\ Fe''(NO_3)_2 + 2\ HNO_3 + S.$

Which equation shows the transformation of chromium in a chromate to chromium as a base? Which equation shows the change of iron from the ferric to the ferrous condition?

NICKEL.

Symbol, Ni''. — Atomic Weight, 58. — Specific Heat, 0.1080. — Melting-Point, nearly a white heat.

304. Occurrence. — Nickel never occurs native, but its ores are usually found in connection with cobalt ores. Meteoric iron always contains nickel. Its chief ores are Kupfer-nickel, NiAs, — which is the most important ore, and which is found in Saxony, Styria, and the United States, — Nickel-glance, $Ni(AsS)_2$; Breithauptite, NiSb; Nickel-blende, NiS. (Also see Cobalt.)

305. Preparation. — Metallic nickel is now obtained mostly in the wet way. The ores are roasted, and then dissolved in hydrochloric acid; this solution usually contains iron, cobalt, and copper, which accompany the nickel in its ores. In such cases the iron salts are oxidized by chlorine and then precipitated by adding limestone; the copper is precipitated by hydrogen sulphide and the cobalt by bleaching-powder. The remaining clear solution contains the nickel, which is now precipitated by the addition of an alkali, usually sodium hydroxide. From the nickel hydroxide thus obtained the nickel is reduced by fusion with charcoal.

306. Properties, Uses, and Salts of Nickel. — Nickel is a white, hard metal, scarcely tarnishing in the air, and susceptible of a brilliant polish. It is accordingly used extensively in coinage and in plating other metals. The salt used in electro-plating is a double sulphate of nickel and ammonium. Its chief alloy is German silver.

SUG. For a valuable paper on Electro-Nickel Plating as an Industry, which gives the history and development of the details of the processes employed in electro-nickel plating, see "Scientific American Supplement" for May 10, 1884, p. 6957.

Nickel, like iron, can be welded, and is likewise attracted by the magnet.

The best solvent for nickel is dilute nitric acid.

THE PRINCIPAL COMPOUNDS OF NICKEL ARE: —

(*a*) *The Oxides*, NiO and Ni_2O_3. We must also note the apple-green hydroxide, $Ni(OH)_2$, which may be obtained by the action of an alkali, as $NaOH$, on a solution of a nickel salt.

(*b*) *Nickel Sulphate*, $NiSO_4 + 7\ H_2O$. Prepared by dissolving the metal or its hydroxide in sulphuric acid.

(*c*) *Nickel Ammonium Sulphate*, $Ni(NH_4)_2(SO_4)_2 + 6\ H_2O$. Obtained by adding ammonium sulphate to nickel sulphate.

(*d*) *Nickel Sulphide*, NiS. Obtained as a black powder by adding ammonium sulphide to an alkaline solution of a nickel salt. It is the *group-reagent precipitate;* it also occurs in nature as Millerite in rhombohedral or capillary crystals.

307. Tests for Nickel. — 1. Nickel compounds in the *oxidizing*-flame give the borax bead a brownish-red color when hot, yellow when cold. In the *reducing*-flame the bead assumes a grayish color owing to the reduction of metallic nickel. The presence of cobalt may obscure this test. See

2. In the wet way the solid is dissolved in water or aqua regia. This solution is then tested for nickel thus: —

(*a*) With a drop or two of ammonia the apple-green hydroxide, $Ni(OH)_2$, is thrown down; but if ammonia be added to excess, the hydroxide dissolves, forming a *blue* solution. Again add potassium hydroxide to this blue solution, and the apple-green precipitate again appears.

(*b*) Add potassium or sodium hydroxide to the original solution, — an apple-green precipitate. In general, all the salts of nickel are greenish.

EXERCISES.

1. Dissolve a nickel three-cent piece in nitric acid, and determine what metals the coin contains.

2. Heat a nickel salt with Na_2CO_3 on charcoal. Does a magnet attract the powder obtained? What other substance (metallic oxide) is thus attracted?

3. Read R. & S., Vol. II., Pt. II., pp. 146–149, on the alloys of nickel.

Prepare $Ni(NO_3)_2$ and $NiSO_4$, and describe the processes, etc., as experiments.

COBALT.

SYMBOL, Co''. — ATOMIC WEIGHT, 59. — SPECIFIC HEAT, 0.10674. — MELTING-POINT, A WHITE HEAT.

308. Occurrence. — Cobalt does not occur free, and its ores are neither plentiful nor widely distributed. Some of its ores are Speiss Cobalt, $Co(Ni,Fe)As_2$; Skutterrudite, $CoAs_3$; and Cobalt-glance, $CoFeAs_2S_2$.

309. Preparation. — Metallic cobalt is of little or no use in the arts, and is prepared in small quantities only for scientific purposes. The metal is reduced by strongly heating the oxide or chloride of cobalt in an atmosphere of hydrogen, when the cobalt is obtained as a gray, metallic powder.

The metal can also be obtained in a coherent state by fusing its oxalate under a layer of powdered glass and afterwards fusing the metal in a graphite crucible.

310. Properties and Compounds of Cobalt. — Coherent metallic cobalt resembles iron in its whitish color and in being attracted by the magnet. It oxidizes but slowly when in the coherent condition, but when in the form of a powder it oxidizes quickly at ordinary temperatures.

The compounds of cobalt are valuable, and are prepared directly from the arsenical ores, preferably speiss cobalt, $Co(Ni,Fe)As_2$.

The ore is roasted to vaporize the arsenic, then fused with lime and sand to remove the iron. The residue is now dissolved in hydrochloric acid, and any remaining impurities are precipitated by adding successively chlorine calcium carbonate, and hydrogen sulphide. The remaining solution is thus freed from all the first and second group metals, the cobalt only remaining in solution.

The oxide of cobalt is obtained from this solution by the aid of bleaching-powder. The oxide is an article of commerce, and is used for coloring glass blue, and for preparing the salts and compounds of cobalt, which are of great value as pigments.

There are two series of cobalt salts, — the *cobaltous* and *cobaltic*. In the latter series, the salts are of a varying formula, and not of sufficient importance to warrant a notice here. The cobalt salts are violet when anhydrous, and pink in color when hydrated; hence they are used to make "sympathetic ink," which becomes visible upon warming.

Cobalt or its oxides, CoO and Co_2O_3, are soluble in dilute HNO_3.

THE PRINCIPAL COBALT SALTS ARE:—

(*a*) *Cobaltous Chloride*, $CoCl_2$. Prepared by dissolving the metal or its carbonate in hydrochloric acid; it is used as a sympathetic ink.

(*b*) *Cobaltous Nitrate*, $Co(NO_3)_2$. Prepared by dissolving the metal or its carbonate in dilute nitric acid; it is used as a reagent.

(*c*) *Cobaltous Sulphide*, CoS, *the group-reagent precipitate.* A black precipitate obtained by adding ammonium sulphide to a solution of a cobalt salt.

(*d*) *Silicates of Cobalt.* These are prepared artificially, and are known as "Smalt." The ore is first roasted sufficiently to oxidize the cobalt, and then fused with quartz and potash, when a dark-blue glass is formed, which is crushed into dust, under water, by granite millstones, and is sold as a pigment.

(*e*) *Rinmann's Green.* A pigment prepared by precipitating a solution of zinc and cobalt sulphates by sodium hydroxide. This precipitate is then heated and reduced to an impalpable powder. Its formula is unknown.

(*f*) *Thenard's Blue*, or *Cobalt Ultramarine.* A valuable pigment prepared by heating alumina with a cobalt salt. Its formula varies.

311. Tests for Cobalt.—1. Any cobalt compound colors the borax or microcosmic bead blue,—often appearing black when the cobalt is in excess; when powdered, the dust obtained from the bead is blue in all cases.

Note. Should iron or nickel compounds be present, they may be reduced to a colorless condition (metallic) by the continued application of the reducing-flame, so that they will not interfere with this test.

312. To separate and identify Nickel and Cobalt. — To a somewhat concentrated solution of the salts of these two metals add acetic acid and potassium nitrite (KNO_2). Warm the solution gently for some time, and allow it to stand for about twenty-four hours. At the end of this time a yellow, crystalline precipitate of potassium-cobaltic nitrite will settle.

(*a*) Obtain the nickel test from the solution. (Art. 307.)

(*b*) Apply the cobalt test (Art. 311) to the precipitate.

Sug. Read the "Chemical News" for April 10, 1885, p. 170, for a new method of separating nickel and cobalt.

MANGANESE.

SYMBOL, Mn''. — ATOMIC WEIGHT, 55. — SPECIFIC HEAT, 0.1217. — MELTING-POINT, A WHITE HEAT.

313. Occurrence. — Manganese never occurs free. Its chief ore is Pyrolusite, MnO_2; it also occurs in Braunite, Mn_2O_3, Hausmannite, Mn_3O_4, Rhodocrosite, $MnCO_3$, and Manganite, $Mn_2O_2(OH)_2$.

314. Preparation. — Metallic manganese is not employed for practical purposes. It is obtained by fusing, at a white heat, a mixture of any one of its oxides and charcoal in a closed crucible lined with graphite.

315. Properties and Compounds of Manganese. — Manganese is a reddish-white, brittle metal, oxidizing so easily in the air that it must be kept under naphtha or coal-oil.

THE IMPORTANT COMPOUNDS OF MANGANESE ARE: —

(*a*) *The Oxides.* — *Manganous Oxide*, MnO. A grayish-green powder.

Manganoso-Manganic Oxide, or *Red Oxide of Manganese*, Mn_3O_4. This substance crystallizes in acute, quadratic pyramids.

Manganic Oxide, Mn_2O_3. This oxide is brownish-black, and crystallizes in obtuse quadratic pyramids. As it occurs in nature it is known as Braunite.

Manganese Dioxide, or *Black Oxide of Manganese*, MnO_2. This is the most important of the manganese oxides. It is used in the laboratory in many ways, but its principal use is for preparing chlorine gas, thus:—

$$MnO_2 + 4\ HCl = MnCl_2 + 2\ H_2O + Cl_2.$$

The chloride, $MnCl_2$, is not a waste product, since it may be again converted into the dioxide: —

(1) $MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2;$

(2) $MnCO_3 + O$ (heated in a blast of hot air) $= MnO_2 + CO_2.$

This illustrates a process employed in generating chlorine for the manufacture of bleaching-powder.

Manganese Heptoxide, Mn_2O_7, is a dark, reddish-brown liquid, which yields, with water, permanganic acid: $Mn_2O_7 + H_2O = 2\ HMnO_4$.

The other oxides of manganese are basic oxides; of these MnO is the strongest base.

(*b*) *Manganic Acid*, H_2MnO_4, and *Permanganic Acid*, $HMnO_4$. The first is a very unstable acid not known in the free state; its salts, the manganates, are green in color, and very unstable, except in the presence of an excess of alkali.

Permanganic acid is prepared thus: —

$$Ba(MnO_4)_2 + H_2SO_4 = 2\ HMnO_4 + BaSO_4.$$

This acid in aqueous solution is a deep-red liquid possessing a bitter, metallic taste; it is readily decomposed by heat or exposure to light. Of its salts the principal one is

Potassium Permanganate, $KMnO_4$ or $K_2Mn_2O_8$. This is a crystalline substance, the color of which varies through green, black, and steel-blue, depending upon the age and exposure of the crystals. The uses of the permanganate are numerous, with many of which the student is already acquainted. Organic substances, as in drinking-water, reduce permanganates to lower compounds, partially manganates.

Condy's Disinfecting Liquid is obtained by dissolving the permanganate in water. The commercial article, however, is not a pure permanganate, and is prepared on the large scale by heating to redness for several hours caustic soda with manganese dioxide; the fused substance is then lixiviated with water, and the solution is afterwards concentrated, when it is ready for the market.

Exp. 163 t. *Chameleon Mineral* is a remarkable compound which may be readily prepared as follows: Fuse in a crucible equal weights of solid potassium hydroxide and finely levigated manganese dioxide. Fill a tall jar with pure water, and slowly drop in the powdered and cooled mass formed by fusion. Note the colors obtained as the fine particles find their way to the bottom of the vessel.

Note. The chemical changes which take place in this experiment are, first, the formation of a salt of the composition K_2MnO_4, potassium manganate,

$$3\,MnO_2 + 2\,KOH = K_2MnO_4 + Mn_2O_3 + H_2O,$$

the solution of which is green. This salt is unstable unless free alkali is present. When poured into water it is converted into the permanganate, $K_2Mn_2O_8$ (or $KMnO_4$), the solution of which has a beautiful purplish-red color. Hence, in the above experiments, the color changes from green to purplish-red, and various intermediate colors are observed.

(*c*) *Manganese Sulphide*, MnS, is the flesh-colored *group-reagent precipitate* obtained by ammonium sulphide in an alkaline solution of any salt of manganese. It also occurs as the mineral Alabandite, or Manganese Blende, in cubical or octahedral, steel-gray crystals.

316. Tests for Manganese. — 1. To the borax and microcosmic beads in the oxidizing-flame manganese gives a violet color when hot, amethyst-red when cold.

In the reducing-flame the bead becomes colorless.

2. When fused on platinum foil with Na_2CO_3 and KNO_3, manganese compounds give a bright-green mass, (what?). Dissolve this mass in water and add HNO_3; a red solution is formed.

3. The manganese acids may be distinguished by the color of their salts in solution, and by further yielding the reactions in 1 and 2.

What substances bleach a permanganate?

ZINC.

SYMBOL, Zn''. — ATOMIC WEIGHT, 65. — SPECIFIC HEAT, 0.0955. — MELTING-POINT, 423° C.

317. Occurrence. — Zinc seldom or never occurs native. Its chief ore is Smithsonite, or $ZnCO_3$. Franklinite, $(Zn, Fe)O + Fe_2O_3$; Zinc blende, ZnS; Willemite, Zn_2SiO_4, and a red oxide which owes its color to a reddish oxide of manganese, are the ores chiefly employed in the reduction of zinc in the United States.

318. Preparation. — The ores of zinc are first roasted and ground fine, then mixed with coal-dust to the amount of one-half their weight. This mixture is then placed in clay retorts, and heated until the zinc is reduced and vaporized, when the escaping vapors are condensed in iron condensers. Zinc thus prepared is the commercial article, and is seldom pure, since it contains small quantities of carbon and iron, lead, arsenic, antimony, and other metals.

319. Properties, Uses, and Salts of Zinc. — Zinc is a malleable, ductile, bluish-white metal which is used for many purposes. Its uses in our dwellings are familiar to all. It is also used, when alloyed with copper to form brass, in ways innumerable. In the laboratory, zinc is used in batteries, in preparing hydrogen, in desilvering lead, and in reducing other metals from their solutions. Sheet iron, when covered with a coating of zinc, is said to be galvanized.

SUG. Let the student name the metals which he can obtain from solutions of their salts by suspending a strip of zinc therein.

In the form of dust, zinc is used in chemistry as a reducing agent. Zinc-dust burns in the Bunsen flame with a white bluish light.

Pure zinc dissolves very slowly in sulphuric acid, hence it is well to add a small quantity of platinum chloride to the granulated zinc employed by the student. Cover the zinc with water, pour in the platinum chloride, and a coating of platinum black is soon deposited on the zinc. Now, when the sulphuric acid is poured in, a galvanic current is established, and the zinc readily dissolves. A solution of pure copper sulphate answers the same purpose.

Zinc salts, when taken internally, are poisonous. Canned goods may become poisonous when the tin cans are soldered by the aid of zinc chloride, which is a soldering fluid often employed by tinners.

SUG. Read the "Chemical News," June 5, 1885, p. 268, for valuable information concerning poisoned canned goods.

THE PRINCIPAL COMPOUNDS OF ZINC ARE: —

(*a*) *Zinc White*, ZnO. Used as a paint.

(*b*) *Zinc Chloride*, $ZnCl_2$. Used as a caustic in surgery, and in organic chemistry for removing the elements of water from many substances. It is also used in "weighting" cotton goods.

(*c*) *Zinc Sulphate*, or *White Vitriol*, $ZnSO_4 + 7\,H_2O$. Used in medicine and in dyeing.

(*d*) *Zinc Sulphide*, ZnS, the *group-reagent precipitate* (white).

320. Tests for Zinc. — 1. Unknown solids are tested for zinc by the blowpipe. When heated in the oxidizing flame on charcoal, zinc compounds with Na_2CO_3 give a coating around the assay, which is *yellow* when hot, *white* when cold.

2. If after being treated as in 1, the mass be moistened with cobaltous nitrate and heated again, it turns *green*. This color is a beautiful one, known as Rinman's green.

3. Solutions are first made alkaline, and ZnS (white) is precipitated with $(NH_4)_2S$. This sulphide is insoluble in dilute acetic acid, and is further tested by 1 and 2.

321. To separate and identify Nickel, Cobalt, Manganese, and Zinc. — Obtain the precipitates NiS, CoS, MnS, and ZnS, as directed in Art. 290. Warm the test-tube containing the precipitate until the sulphides settle; then filter out and wash this precipitate and wash it through into a test-tube; dissolve as much of it as possible with cold dilute HCl. Any residue may be NiS or CoS, or both; filter and test as in (*a*). The filtrate is tested by (*b*) for manganese and zinc.

(*a*) This residue is always black when containing Ni or

Co, or both metals. Test it by the borax bead. (See Arts. 307, 1 and 2, and 311, 1, note.) It is well, also, to proceed by 312 to make sure whether both are present.

Note. Some free sulphur usually remains on the paper with this residue. Whence came it?

(*b*) Boil to expel H_2S, and add a decided excess of KOH to the hydrochloric acid solution in a test-tube. Allow it to stand some time, and shake it frequently. If manganese be present, it will be precipitated as $Mn(OH)_2$, when it must be filtered out, and tested by Art. 316, 2.

Note. Test this precipitate also for Ni and Co, since the HCl is apt to dissolve small portions of their sulphides.

For detecting the zinc, acidify with acetic acid the filtrate just obtained, and add $(NH_4)_2S$, — a white precipitate, ZnS. Also test by Art. 320, 1 and 2.

General Note. Phosphoric acid or phosphates, when present in third and fourth group solutions, cause them both to be precipitated with $(NH_4)_2S$. For separation of third and fourth group metals in presence of phosphates, see Douglas and Prescott's "Qual. Anal.," p. 241.

SOME REACTIONS IN GROUP III.

Balance and explain these equations: —

(1) $Fe + H_2SO_4 = FeSO_4 + H$.
(2) $Fe +$ (cold dil.) $HNO_3 = Fe(NO_3)_2 + NH_4NO_3 + H_2O$.
(3) $Fe +$ (hot dil.) $HNO_3 = Fe_2(NO_3)_6 + NO + H_2O$.
(4) $Fe + HCl = FeCl_2 + H$.
(5) $FeCl_2 + Cl = Fe_2Cl_6$.
(6) $Fe + HNO_3$ (cold, very dil.) $= Fe(NO_3)_2 + H$.
(7) $Fe_2Cl_6 + H_2S = FeCl_2 + HCl + S$.
(8) $FeSO_4 + (NH_4)_2S = \underline{FeS} + (NH_4)_2SO_4$.
(9) $Fe_2Cl_6 + KOH = \underline{Fe_2(OH)_6} + KCl$.
(10) $Al + H_2SO_4 = Al_2(SO_4)_3 + H$.

(11) $Al + HCl = Al_2Cl_6 + H.$

(12) $Al_2Cl_6 + (NH_4)_2S + H_2O = \underline{Al_2(OH)_6} + NH_4Cl + H_2S.$

(13) $K_2Cr_2O_7 + (NH_4)_2S_2 + H_2O = \underline{Cr_2(OH)_6} + K_2SO_3 + NH_3 + S.$

(14) $MnO_2 + HCl = MnCl_2 + Cl + H_2O.$

(15) $MnO_2 + H_2SO_4 + NaCl = MnSO_4 + Na_2SO_4 + Cl_2 + H_2O.$

(16) $MnSO_4 + (NH_4)_2S = \underline{MnS} + (NH_4)_2SO_4.$

(17) $Co + HNO_3 = Co(NO_3)_2 + H_2O + NO.$

(18) $CoNO_3 + (NH_4)_2S = CoS + (NH_4)NO_3.$

(19) $CoCl_2 + KNO_2 + HC_2H_3O_2 + H_2O = \underline{(KNO_2)_6, Co_2O(NO_2)_4},$
$H_2O + KCl + NO + KC_2H_3O_2.$

(20) $Ni + HCl = NiCl_2 + H.$

(21) $Ni + HNO_3 = Ni(NO_3)_2 + H_2O + NO.$

(22) $NiCl_2 + (NH_4)_2S = \underline{NiS} + NH_4Cl.$

(23) $NiCl_2 + KOH = Ni(OH)_2 + KCl.$

(24) $Zn + H_2SO_4 = ZnSO_4 + H.$

(25) $Zn + HCl = ZnCl_2 + H.$

(26) $ZnSO_4 + (NH_4)_2S = \underline{ZnS} + (NH_4)_2SO_4$

(27) $ZnCl_2 + KOH = Zn(OH)_2 + KCl.$

QUERY. Are all of the metals of the third group precipitated with ammonium sulphide?

SUG. Separate and identify Ni and Co thus: To a solution of their salts add KCy until the precipitate at first formed dissolves; slightly acidulate with HCl, and boil some time; a little HCl now precipitates $NiCy_2$.

THE RARE METALS OF GROUP III.

BERYLLIUM.

SYMBOL, BE. — ATOMIC WEIGHT, 9.

322. Beryllium, also known as Glucinum, is a silver-white metal occurring in Beryl, $Be_3Al_2Si_6O_{18}$.

It is prepared by fusing $BeCl_2$ with metallic sodium or potassium.

The salts of beryllium have a sweetish taste, from which fact the metal first received the name glucinum.

In the regular course of analysis beryllium is obtained along with aluminum, from which metal it *can be separated* by precipitation with $(NH_4)_2CO_3$.

INDIUM.

SYMBOL, IN. — ATOMIC WEIGHT, 113.6.

323. Indium occurs in zinc blende, and was discovered by means of the spectroscope. It is a soft, white metal which scarcely undergoes any change in the air. It is prepared from its ores in the wet way.

Indium is detected by moistening its compounds with hydrochloric acid; then it is placed in the non-luminous Bunsen flame by means of a looped platinum wire. It colors the flame blue.

GALLIUM.

SYMBOL, GA. — ATOMIC WEIGHT, 69.

324. This metal also occurs in zinc blende, and was discovered by the spectroscope. Its more prominent properties were predicted previous to its discovery by Mendelejeff, under the name of "Ekaluminum." (See p. 222.) It is prepared in the wet way, and is a bluish-white metal, oxidizing readily in the air, and melting at the extremely low temperature of 30.1° C.

It is *detected* by the spectroscope. Its luminous spectrum contains two violet lines.

NOTE. The luminous spectrum is obtained by igniting a substance on platinum wire in the Bunsen flame, or by means of a powerful current of electricity, and exposing the flame directly to the spectroscope. The absorption spectrum is obtained by igniting as above, and placing a luminous gas-flame or other absorbing material between the burning metal and the spectroscope. The spark spectrum is obtained by moistening the carbon terminals of a dynamo or other powerful electric machine with a solution of the substance to be tested, after which sparks are allowed to pass.

YTTRIUM.

SYMBOL, Yt. — ATOMIC WEIGHT, 89.

325. Yttrium occurs along with erbium.

It is detected by the spark spectrum of its chloride, which gives many bright lines, of which the most marked are two groups near the sodium line.

LANTHANUM.

SYMBOL, La. — ATOMIC WEIGHT, 138.2.

326. Lanthanum occurs in the mineral Lanthanite as $La_2(CO_3)_3 + 8\,H_2O$. It is best prepared by the electrolysis of its chloride, and is a soft grayish metal which readily tarnishes in the air, assuming a steel-blue tint. *It is detected* by its spark spectrum containing many characteristic lines.

CERIUM.

SYMBOL, Ce. — ATOMIC WEIGHT, 141.

327. Cerium occurs along with Lanthanum, and is similarly prepared. It is a soft, gray metal which tarnishes in damp air, assuming, successively, the colors yellow, blue, and green.

It burns with great brilliancy when heated in the air, and *is detected* by its spark spectrum which contains three bright lines in the green.

DIDYMIUM.

SYMBOL, Di. — ATOMIC WEIGHT, 142.3.

328. This metal occurs along with the rare metals previously mentioned, and is prepared similarly to Lanthanum. It has a yellowish lustre, and burns brightly when heated in the air.

It is detected by its absorption spectrum. Its salts have a rosy tint, and it colors the microcosmic bead rose-red.

TERBIUM.

SYMBOL, TB. — ATOMIC WEIGHT, 148.5.

329. This metal has not been prepared, but its oxide, Tb_2O_3, is an orange-yellowish powder. It is difficult to separate terbium from the preceding kindred metals, and no sure means of detection is known, since it gives no absorption spectrum.

ERBIUM.

SYMBOL, ER. — ATOMIC WEIGHT, 166.

330. This metal occurs with the foregoing, and has not been obtained pure. *It is detected* by its continuous luminous spectrum, which is crossed by bright lines which are darkened in the same position in the absorption spectrum.

THORIUM.

SYMBOL, TH. — ATOMIC WEIGHT, 232.

331. Thorium occurs in Thorite and other complex minerals, and is prepared by heating its chloride with potassium. This metal as thus prepared is a gray powder which burns brightly in the air.

Thorium is detected by the precipitation of its carbonate or hydroxide; these are soluble in an excess of the precipitant.

TITANIUM.

SYMBOL, TI. — ATOMIC WEIGHT, 48.

332. This metal occurs in Rutile and in Titanite, $TiCaSiO_5$, and other minerals. It forms a considerable per cent of some of the Lake Superior iron ores. Titanium is prepared by heating a double fluoride of potassium and titanium in a closed crucible with metallic potassium; the fused mass is then lixiviated with water, when the titanium remains as a dark-gray powder.

At a high temperature this metal unites directly with nitrogen, — a marked peculiarity; it also burns when heated in the air. In blast furnaces, when reducing iron ore containing titanium, a peculiar compound, Titanium Cyano-nitride, $TiCy_2 + 3\ Ti_3N_2$, is obtained.

Titanium is detected by imparting to the microcosmic bead in the reducing-flame a yellow color when hot, violet when cold; when iron is present the bead is red. The oxidizing-flame gives no color.

ZIRCONIUM.

SYMBOL, ZR. — ATOMIC WEIGHT, 90.

333. Zirconium occurs in the mineral Zircon, $ZrSiO_4$, and is prepared in the same way as titanium, which metal it strongly resembles. The amorphous form burns easily, but a crystalline variety takes fire in the air only at the highest temperatures.

Zirconium is detected by precipitating its sulphate by K_2SO_4, which gives a basic salt insoluble in water and hydrochloric acid. Its spectrum is characteristic.

URANIUM.

SYMBOL, U. — ATOMIC WEIGHT, 239.8.

334. Uranium occurs in pitch blende, U_3O_8, and is prepared in the wet way, or by fusing its chloride with potassium.

This is a hard, grayish-white metal, which also burns in the air.

The black oxide, U_2O_5, is used for painting on porcelain. The uranium salts are fluorescent, and impart this property to "canary" glass.

Uranium is detected by its giving to the microcosmic bead in the oxidizing-flame a yellow color when hot, green when cold; when farther heated the color is darkened.

The spectrum of uranium is distinctive.

TANTALUM.

SYMBOL, TA.—ATOMIC WEIGHT, 182.

335. Tantalum occurs together with many of the rare metals previously noticed, but more especially with niobium, from which metal it has not been separated.

Tantalite, Columbite, Pyrochlor, Yttrotantalite, Pitch Blende, and many other minerals contain small quantities of this metal. Tantalum has not been obtained pure.

It is detected by converting the compound into tantalic acid, and adding potassium ferrocyanide to its solution; this yields a yellow precipitate. The conversion is effected by heating the compound with carbon in a current of chlorine to obtain the chloride $TaCl_5$; this chloride, when mixed with water, yields the acid $HTaO_3$. A solution of nut-galls gives a yellow precipitate with solutions of this acid.

NIOBIUM.

SYMBOL, Nb. — ATOMIC WEIGHT, 94.

336. Niobium occurs with Tantalum, and is prepared by passing the vapor of its chloride and hydrogen through a red-hot porcelain tube. It is a steel-gray metal, burning easily in the air.

Niobium is detected similarly to tantalum, the precipitate with K_4FeCy_6 being brown; with nut-galls solution, orange-red.

VANADIUM.

SYMBOL, V. —ATOMIC WEIGHT, 51.5.

337. This metal occurs in Vanadanite, $3\ Pb_3(VO_4)_2 + PbCl_2$, and is prepared as a grayish powder by heating its chloride in hydrogen.

Vanadium bronze, or metavanadic acid, is now used in place of gold bronze for gilding.

Vanadium is detected by placing a strip of zinc in a solution of vanadium chloride; the solution turns blue. When hydrogen dioxide and ether are added to the solution of a vanadate, the solution turns red.

GENERAL NOTE. Observe those formulae like $Co(Ni, Fe)As_2$; these do not signify that both Ni and Fe are present, but that one or the other is found in such a compound.

CHAPTER XVIII.

THE FOURTH GROUP METALS.

338. The fourth group metals are commonly known as the Metals of the Alkaline Earths.

Their chlorides, hydroxides, and sulphides are soluble in water, acids, and alkalies. In the course of analysis they are precipitated as carbonates by ammonium carbonate, $(NH_4)_2CO_3$, in the presence of ammonia and ammonium chloride. We must except magnesium, however, from the above statement, since its carbonate is soluble in ammonium compounds. It is best to filter out the precipitates obtained by ammonium carbonate, and to precipitate the magnesium from the filtrate by means of di-sodium phosphate, Na_2HPO_4.

THE FOURTH GROUP METALS ARE:—

DIVISION A	Barium, Ba. Strontium, Sr. Calcium, Ca.	DIVISION B	Magnesium, Mg.

These metals oxidize easily in the air, and consequently never occur free; they are strongly basic, hence they are not easily reduced to a metallic state; they form no acids; they decompose water to form alkaline hydroxides.

BARIUM.

SYMBOL, BA$''$. — ATOMIC WEIGHT, 137. — SPECIFIC HEAT, ——. MELTING-POINT, HIGHER THAN CAST IRON.

339. Occurrence. — The most abundant ore of this metal is Heavy Spar, $BaSO_4$. Barium also occurs in small quantities in Witherite, or $BaCO_3$, in certain silicates in feldspathic rocks, in seaweeds, and in mineral waters.

340. Preparation. — Barium amalgam is prepared by electrolyzing a thick paste of $BaCl_2$ and dilute HCl in the presence of mercury. This amalgam is then heated to vaporize the mercury, thus leaving a porous mass of metallic barium. Barium oxidizes rapidly in the air, and burns with great brilliancy.

341. Compounds and Uses of Barium. — Metallic barium is not used in the arts.

ITS PRINCIPAL COMPOUNDS ARE: —

(*a*) *Barium Monoxide*, or *Baryta*, BaO, which is prepared by heating the nitrate until nitrous fumes cease escaping.

Barium Hydroxide, or *Caustic Baryta*, $Ba(OH)_2$, is obtained by moistening BaO with water; a solution of this hydroxide is used as a reagent known as Baryta Water. Caustic baryta is now largely used in refining cane sugar, which it precipitates from its impure solutions as $C_{12}H_{22}O_{11}BaO$. The barium is afterwards removed by treatment with carbon dioxide gas, which precipitates the insoluble compound, $BaCO_3$, while the sugar dissolves.

Barium hydroxide is now prepared in large quantities by passing moist carbon dioxide gas through heated barium sulphide, which gives $BaCO_3$; this carbonate is then treated with superheated steam, when this reaction occurs: —

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2.$$

(*b*) *Barium Chloride*, $BaCl_2$. This salt is used as a reagent to detect and estimate sulphuric acid; it is prepared by dissolving barium carbonate, $BaCO_3$, in hydrochloric acid. Write the equation.

(*c*) *Barium Iodate*, $Ba(IO_3)_2$, which is used to prepare iodic acid, HIO_3; this iodate is prepared thus: —

$$BaCl_2 + 2\ KIO_3 = Ba(IO_3)_2 + 2\ KCl.$$

(*d*) *Barium Sulphate*, or *Heavy Spar*, $BaSO_4$. This mineral is an important barium ore, used for weighting paper and as a paint. It is prepared for commerce thus: —

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2\ HCl.$$

(*e*) *Barium Nitrate*, $Ba(NO_3)_2$. This is prepared thus: —

$$BaCO_3 + 2\ HNO_3 = Ba(NO_3)_2 + H_2O + CO_2.$$

It is used in making green fires for tableaux and pyrotechnics.

(*f*) *Barium Carbonate*, $BaCO_3$, which occurs in nature as *Witherite;* it is also the *group-reagent precipitate*, prepared by precipitating a barium salt by means of an alkaline carbonate. It is largely used to prepare soluble barium salts.

342. Tests for Barium. — 1. Solids are fused with sodium carbonate, if necessary, and then dissolved in hydrochloric or nitric acid; this solution gives these precipitates: —

(*a*) With $K_2Cr_2O_7$ and ammonia, a yellow precipitate, $BaCrO_4$, insoluble in acetic acid.

(*b*) With H_2SO_4, a white precipitate, $BaSO_4$, insoluble in acids.

(*c*) $CaSO_4$ gives an immediate precipitate of $BaSO_4$ even in dilute solutions.

2. Barium salts tinge the non-luminous flame green.
3. The barium spectrum, although complicated, is readily distinguished by the green lines Baα and Baβ.

STRONTIUM.

SYMBOL, SR''. — ATOMIC WEIGHT, 87.2. — MELTING-POINT, A RED HEAT.

343. **Occurrence.** — Strontium occurs most plentifully in the two ores, Celestine, $SrSO_4$, and Strontianite, $SrCO_3$. It also occurs in a few mineral waters and in sea-water.

344. **Preparation.** — This metal is prepared by electrolyzing its chloride, or by heating this compound with a sodium amalgam; the strontium amalgam thus formed is then washed, dried, and, finally, ignited in a current of hydrogen.

345. **Properties, Compounds, and Uses of Strontium.** — Strontium is a yellow, malleable metal, oxidizing in the air, and burning brightly when heated.

THE PRINCIPAL STRONTIUM COMPOUNDS ARE: —

(*a*) *Strontium Carbonate*, $SrCO_3$. This precipitate is obtained by precipitating a strontium salt solution with an alkaline carbonate.

(*b*) *Strontium Nitrate*, $Sr(NO_3)_2$. This is prepared thus: —

$$SrCO_3 + 2\ HNO_3 = Sr(NO_3)_2 + H_2O + CO_2.$$

It is used in producing red fire for tableaux, etc. Material for red fire is best produced by mixing about equal parts of finely pulverized and thoroughly dried $Sr(NO_3)_2$ and $KClO_3$ with an equal bulk of powdered shellac, or with one-fourth part flowers of sulphur; the shellac is preferable, as it gives off no suffocating fumes of sulphur dioxide. Green fire is obtained similarly, by using barium nitrate, $Ba(NO_3)_2$, in place of strontium nitrate.

Caution. These ingredients must be powdered separately, and afterwards mixed with a bone knife on paper, since any concussion may produce an explosion.

346. Tests for Strontium. — 1. Most strontium compounds, when moistened with hydrochloric acid, impart a beautiful crimson tint to the non-luminous flame. Sulphates should be reduced to sulphides in the reducing-flame and then moistened with HCl before ignition.

Note. When both barium and strontium are present, the strontium color appears when the substance is first brought into the flame. A caution, also, is needed here lest the student mistake the pale yellowish-red flame of calcium for that of strontium. Compare the colors yielded by the pure salts of these two metals.

2. The spectrum of strontium contains the prominent lines: Srα, orange; Srβ, red; and Srδ, blue.

3. In the wet way, strontium when precipitated with carbonates, phosphates, and oxalates, resembles barium. It may be separated from barium by precipitating the latter with ammonia and $K_2Cr_2O_7$. It may be separated from calcium by precipitating strontium with $CaSO_4$.

CALCIUM.

Symbol, Ca''. — Atomic Weight, 40. — Specific Heat, 0.1804. — Melting-Point, a red heat.

347. Occurrence. — The most abundant compound of calcium is the carbonate, $CaCO_3$. This mineral occurs in enormous quantities and widely distributed; uncrystallized $CaCO_3$ occurs as limestone and chalk; the crystallized forms are many, such as marble, Iceland Spar, Calc Spar, and Dog-tooth Spar. Shells and corals are chiefly carbonates of calcium, while bones and teeth are principally phosphates of this metal. Calcium Sulphate, $CaSO_4$, occurs in Gypsum, Anhydrite, and Selenite. Some mountain ranges and geological formations are chiefly composed of these calcium compounds.

348. Preparation. — This metal is prepared by electrolyzing its chloride, or by fusing calcium iodide with metallic sodium in closed iron retorts.

349. Properties, Compounds, and Uses of Calcium. — Calcium is a malleable metal, which oxidizes most rapidly in moist air, and burns with an orange-yellow light.

THE MOST USEFUL COMPOUNDS OF CALCIUM ARE: —

(*a*) *Quick-lime*, CaO, prepared by heating the carbonate, $CaCO_3$. Give the equation.

Calcium Hydroxide, $Ca(OH)_2$, which is prepared by treating CaO with water. When this substance is in a dry powder or of the consistency of paste, it is called "slaked lime." Why? A saturated water solution of calcium hydroxide, called limewater, is used as a reagent for detecting free carbon dioxide gas.

Slaked lime is used for many purposes, such as for making mortar, purifying illuminating gas, whitewashing, etc. Mortar consists of sand, three to four parts, and lime, one part, thoroughly mixed with water.

SUG. Describe the method of making mortar. (Ask a mason or plasterer, if you do not know.) What is "putty coat" or "hard finish"?

Lime containing about ten per cent of silica is known as hydraulic cement or water-lime, and possesses the peculiar property of hardening under water. This cement is artificially prepared by mixing finely pulverized burnt clay and limestone.

Calcium hydroxide absorbs carbonic acid gas from the air, which fact explains the hardening of the mortar. It may also combine with the silica.

QUERY. Does age improve the hardness of cement or mortar? Does the cement of the ancient Roman masonry owe its stone-like character to its age or to the process of manufacture?

(*b*) *Gypsum*, $CaSO_4 + 2 H_2O$. This occurs native, and when ground is used as land plaster; when calcined, it is known as "Plaster of Paris," which is used in making casts and for filling writing-paper.

QUERY. What is the object of the calcining? Explain the *setting* of the plaster.

(*c*) *Calcium Chloride*, $CaCl_2$. This substance is prepared by dissolving Iceland spar or pure marble in hydrochloric acid. When fused, it is used as a dryer for gases, owing to its great absorptive power for moisture.

(*d*) *Fluor Spar*, CaF_2, a well-known mineral used in preparing fluorine compounds.

(*e*) *Bleaching Powder*. This is an article of commerce, and one of the most useful substances known to the arts. It is made by passing chlorine gas into large chambers, on the floors of which slaked lime is spread. It is used in bleaching paper, rags, cotton goods, etc. This powder affords a convenient source of chlorine, which is liberated by the addition of an acid, as sulphuric or hydrochloric acid.

QUERY. Upon what does the bleaching power of chlorine depend?

(*f*) *Superphosphate of Lime* is a substance obtained by treating bones with sulphuric acid; it is used in preparing phosphorus, and also as a fertilizer. The superphosphate is a mixture of calcium sulphate and acid phosphate.

(*g*) *Calcium Carbonate*, $CaCO_3$, previously mentioned under the carbonates. This substance forms one of the constituents called "hardness" in drinking-water (see p. 49).

When a soap is brought into a hard water, insoluble calcium salts are formed with the organic acids contained in the soap; hence the peculiar, unpleasant feeling experienced on attempting to wash the hands with soap in hard water. All the calcium carbonate in solution must be precipitated before the soap will act in the desired way and form a lather.

Iceland Spar, a beautiful crystalline variety, possesses the property of "double refraction."

350. **Tests for Calcium.** — 1. The volatile calcium salts tinge the flame orange-red.

2. The spectrum shows the green line Caβ and the orange line Caα, which are distinctive.

3. In solutions, calcium may be separated from barium and strontium by precipitating the latter metals with K_2SO_4; to the filtrate ammonia and ammonium oxalate, $(NH_4)_2C_2O_4$, are added; the oxalate gives a white precipitate, CaC_2O_4, which under the circumstances is distinctive.

QUERY. Is calcium sulphate easily soluble in water? Try it.

MAGNESIUM.

SYMBOL, MG.″ — ATOMIC WEIGHT, 24. — SPECIFIC HEAT, 0.245.
MELTING-POINT, 750°.

351. **Occurrence.** — Magnesium ores are found plentifully in many localities, among which we notice: Magnesite, $MgCO_3$; Dolomite, $CaMg(CO_3)_2$; Kieserite, $MgSO_4 + H_2O$; Carnallite, $(Mg, K)Cl_2 + 6\,H_2O$; Spinelle, $MgOAl_2O_3$; Asbestos, $(Mg,Ca)SiO_3$; Talc, $Mg_3H_2(SiO_3)_4$; and Meerschaum, $Mg_2H_2(SiO_3)_3$.

Magnesium sulphate also occurs in certain medicinal springs, while the chloride is a constituent of sea-water.

Magnesium limestone is a double carbonate of calcium and magnesium.

352. Preparation. — Magnesium, like calcium, may be prepared by the electrolysis of its chloride, but the commercial article is obtained by fusing a mixture of the dry chloride, fluor spar, and metallic sodium in a closed crucible. The metal is afterward purified by distillation, and, when in a semi-molten condition, it is pressed into wires, which are flattened finally into ribbons.

353. Properties, Uses, and Compounds of Magnesium. — Magnesium is a silver-white metal, quite permanent in dry air; in damp air, however, its surface becomes coated with oxide. It takes fire readily in any ordinary luminous flame, and burns with a painfully bright and dazzling light, which is very rich in chemical rays. Owing to this important property, magnesium ribbon is now employed in photographing caverns and other objects inaccessible to the sun's rays. This metal is also employed in pyrotechny and signaling. It is further employed in chemical analysis, especially in cases of arsenic poisoning, in place of zinc, since magnesium contains no traces of arsenic.

THE MOST IMPORTANT COMPOUNDS OF MAGNESIUM ARE THE FOLLOWING: —

(*a*) *Magnesia*, MgO, which is prepared by igniting the carbonate, $MgCO_3$. It is used in medicine.

(*b*) *Magnesium Chloride*, $MgCl_2$, is obtained from sea-water and salt springs. It is used in dressing cotton goods.

(*c*) *Epsom Salts*, $MgSO_4 + 7\,H_2O$, are prepared from Kieserite, or by treating $MgCO_3$ with sulphuric acid. It is used in medicine as a cathartic, and is also used in dressing cotton goods.

(*d*) *Magnesium Carbonate*, or *Magnesite*, $MgCO_3$, an ore of magnesium. This is artificially prepared by roasting dolomite, and treating the moistened residue with carbon dioxide gas under pressure; a bicarbonate is thus formed, which is decomposed by means of superheated steam. This compound as thus formed is a white powder, which is an important article of commerce. It is used in medicine; also used as a face-powder.

354. Tests for Magnesium. — 1. After removing the metals of the fourth group by ammonium carbonate, etc., di-sodium phosphate, Na_2HPO_4, when added to the filtrate, throws down a white precipitate, $MgNH_4PO_4$; this forms in a dilute solution after stirring the solution with a glass rod for a few minutes. This precipitate, under the circumstances, is distinctive.

NOTE. The spectrum of magnesium is not a practical test, as it is not very marked at the temperature of the Bunsen flame.

355. Separation and Identification of the Fourth Group Metals. — 1. Make the solution to be tested neutral or slightly alkaline, and then remove the metals of Groups I., II., and III. by the usual methods.

Save the filtrate, and boil for some time to expel free H_2S; filter.

2. Add ammonia, NH_4Cl, and $(NH_4)_2CO_3$ to precipitate barium, strontium, and calcium. Filter out this precipitate, and save it to test by 3; also save the filtrate, and test it by 4 for magnesium.

3. Dissolve this precipitate in acetic acid.

(*a*) Test a small portion of the solution for barium by adding $K_2Cr_2O_7$ and ammonia; a yellow precipitate, $BaCrO_4$, indicates barium. If barium be present, thus remove it from the whole solution. This precipitate may be filtered out and dissolved in hydrochloric acid; then, upon addition of H_2SO_4, the insoluble sulphate, $BaSO_4$, will confirm the test.

(*b*) Test a portion of the filtrate from (*a*) for calcium by Art. 350, 3.

(*c*) Precipitate the calcium and strontium from the filtrate not used in (*b*) by means of ammonia and ammonium carbonate. Filter out the precipitate, and dissolve it in HCl, and expel excess of acid; then add $CaSO_4$. A white precipitate, $SrSO_4$, formed after a few minutes, indicates strontium. Further test this precipitate by 346, 1.

4. To the filtrate from 2 add Na_2HPO_4, and stir for some time with a clean glass rod, if necessary; a white precipitate, $MgNH_4PO_4$, indicates magnesium.

REACTIONS IN GROUP IV.

(1) $CaCl_2 + (NH_4)_2CO_3 = \underline{CaCO_3} + NH_4Cl.$
(2) $Sr(NO_3)_2 + (NH_4)_2CO_3 = \underline{SrCO_3} + NH_4NO_3.$
(3) $BaCl_2 + (NH_4)_2CO_3 = \underline{BaCO_3} + NH_4Cl.$
(4) $MgSO_4 + Na_2HPO_4 = \underline{MgHPO_4} + Na_2SO_4.$
(5) $CaCO_3 + H(C_2H_3O_2) = Ca(C_2H_3O_2)_2 + H_2O + CO_2$
(6) $SrCO_3 + H(C_2H_3O_2) = Sr(C_2H_3O_2)_2 +$
(7) $BaCO_3 + H(C_2H_3O_2) =$
(8) $Ca(C_2H_3O_2)_2 + (NH_4)_2C_2O_4 = \underline{CaC_2O_4} + (NH_4)(C_2H_3O_2).$
(9) $Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O + NH_3 = \underline{BaCrO_4} + KC_2H_3O_2$
$+ (NH_4)_2CrO_4.$
(10) $Ba(C_2H_3O_2)_2 + H_2SO_4 = \underline{BaSO_4} + H(C_2H_3O_2).$
(11) $BaCl_2 + K_2CO_3 = \underline{BaCO_3} + KCl.$
(12) $MgSO_4 + Na_2CO_3 = MgCO_3 +$
(13) $CaCO_3 + HCl = \qquad +$

Sug. The student should do much work with the preceding groups; the quickest way to become acquainted with a substance is to work with it. Unknown solutions give an added zest to the student's desire for mastering processes.

CHAPTER XIX.

THE FIFTH GROUP METALS.

356. The metals of the fifth group are known as the "Metals of the Alkalies." They do not yield precipitates with the usual reagents, since the compounds thus formed are soluble; but they are detected by the color which their compounds impart to the non-luminous flames, or by their spectra.

These metals are POTASSIUM and SODIUM, also the compound AMMONIUM, NH_4; the rare metals are LITHIUM, RUBIDIUM, and CÆSIUM.

Of course ammonium is not to be considered a true metal, but its compounds are alkaline, and it behaves much like metals of this group. In distinction from the other or "Fixed Alkalies," ammonium is termed the "Volatile Alkali," *since most of its salts are volatile.*

The metals of this group form a natural series; they are all acted upon by the moisture of the air, and hence they must be kept under naphtha; all decompose water at ordinary temperatures to form strongly alkaline hydroxides; each one forms but one series of salts, many of which are exceedingly stable and useful.

QUERIES. To what group do these metals belong in Mendelejeff's Table? Which belong to the $\left\{\begin{matrix}\text{odd}\\ \text{even}\end{matrix}\right.$ series? Does Na or K show the more intense action when thrown upon the water?

POTASSIUM.

SYMBOL, K'. — ATOMIC WEIGHT, 39. — SPECIFIC HEAT, 0.1655(?). — MELTING-POINT, 62.5°.

357. Occurrence. — The potassium-bearing compounds are widely distributed; they occur in mineral waters, sea-waters, and all fruitful soils, and are utilized by plants and animals. Sheep excrete, through the skin, potassium and other compounds, termed "Fat" and *Suint.* These compounds are of considerable commercial value; they are retained by the wool, of which, before washing, they constitute nearly one-third part by weight.

Some potassium compounds are the following minerals: Sylvite, KCl; Saltpetre, KNO_3; Orthoclase, $K_2Al_2(Si_3O_8)_2$; Carnallite, $(KMg)Cl_3$; and Alum, $K_2Al_2(SO_4)_4 + 24\ H_2O$.

358. Preparation. — Acid potassium tartrate is first heated in closed iron retorts; in this way, a very intimate mixture of potassium carbonate and carbon is obtained. This mixture is then placed in iron tubes covered with clay, which are afterwards placed in a furnace, and heated to a white heat. Metallic potassium is given off in the form of vapors, which are passed into shallow, box-like condensers placed outside the furnace; in these condensers they are quickly cooled to a liquid state; the liquid potassium then flows out into vessels containing rock oil. (See Fig. 20.)

Formerly frequent explosions occurred, owing to the formation of a black substance, KCO; but this trouble is now obviated by the shallow condensers.

Sir Humphry Davy first prepared potassium by electrolyzing the moistened hydroxide. This marked a new era in chemistry, as the alkalies were previously supposed to be elements; and, moreover, with the discovery of potassium, the discovery of other rare metals became possible.

QUERY. What rare metals are now prepared by the aid of metallic potassium or sodium?

359. Properties, Uses, and Compounds of Potassium. — Potassium is a silver-white metal when first cut, but soon afterward exposes a bluish surface. It is brittle at 0° C., and waxy at ordinary temperatures.

It ignites at a low heat, — often while being cut, — and requires the utmost care while being handled; it must be kept under rock oil or naphtha. It quickly decomposes water, liberating hydrogen with such violence that it frequently takes fire and explodes.

It dissolves in ammonia, forming a blue solution, from which it may be again obtained unchanged. The principal use of metallic potassium, other than for class demonstration, is in preparing the rare metals, as previously noticed.

THE PRINCIPAL POTASSIUM COMPOUNDS NOT HERETOFORE NOTICED ARE: —

(*a*) *Potassium Hydroxide,* or *Caustic Potash,* KOH. This is prepared by treating potassium carbonate with slaked lime, thus: —

$$K_2CO_3 + Ca(OH)_2 = 2\ KOH + CaCO_3.$$

The aqueous solution thus prepared is evaporated to dryness, fused, and marketed. In this condition, it is extensively used as a lye. It is purified for reagent purposes by dissolving the crude salt in alcohol, and, after evaporation, again fusing and casting it into sticks. It is kept in air-tight bottles, since it has a powerful attraction for carbon dioxide and moisture, and soon deliquesces; neither must it be handled with the hands, since it destroys the skin.

SUG. Leech some common wood ashes by passing water through them. Examine the filtrate obtained.

(*b*) *Potassium Chloride*, KCl, occurs naturally as Sylvite, and in many brines. It is used as a fertilizer and in preparing other potassium salts.

(*c*) *Potassium Bromide*, KBr. This salt is obtained together with bromate of potassium by dissolving bromine in potassium hydroxide; the bromate is afterwards decomposed by a gentle heat. It is used in medicine as a sedative, and in the laboratory as a source of bromine for demonstration.

QUERY. How is Br prepared?

(*d*) *Potassium Iodide*, KI, may be prepared in the same way as the bromide. It is used extensively in medicine and for other purposes; in the laboratory it is a source of iodine for purposes of demonstration and is a reagent.

SUG. The potassium salts will be found in the laboratory; let the student examine them, note the forms of the crystals, etc., and write a description.

(*e*) *Potassium Chlorate*, $KClO_3$, is obtained by passing a current of chlorine gas through a solution of caustic lime until calcium chlorate, $Ca(ClO_3)_2$, is formed; potassium chloride is then added with the following results: —

$$Ca(ClO_3)_2 + 2\ KCl = 2\ KClO_3 + CaCl_2.$$

The chlorate of potassium is obtained from this solution by crystallization. This salt is used in medicine for inflammation of the throat, and in the laboratory as a source of oxygen.

QUERY. How is oxygen obtained from $KClO_3$? How may potassium chlorate be prepared from chlorine and potassium hydroxide? How is $KClO_4$ prepared? (See Perchloric Acid.)

(*f*) *Potassium Sulphate*, K_2SO_4, occurs native, and is prepared as a by-product in the manufacture of other potassium compounds, as the bichromate, etc. It is used in medicine as a purgative; it is further used in the manufacture of alum, and in the laboratory as a reagent.

An acid sulphate, $KHSO_4$, is obtained in manufacturing nitric acid.

SUG. Write the equation.

(*g*) *Saltpetre*, or *Nitre*, KNO_3, occurs as an incrustation on the soil of some hot, dry climates, as in India and in Egypt, where it is produced by the oxidation of nitrogenous organic substances in contact with the potassium compounds contained in the soil. It has recently been shown that the formation of nitrates which takes place in the soil is caused by minute organisms or ferments. The process is similar to the familiar fermentation of sugar, which causes the formation of alcohol and carbon dioxide.

It is artificially prepared by treating sodium nitrate, which occurs native in immense deposits, with potassium chloride, thus: —

$$NaNO_3 + KCl = KNO_3 + NaCl;$$

and also in the so-called "saltpetre plantations." These are constructed by piling up refuse animal matter, mixed with wood ashes and lime, and moistening with urine or stable drainings. At intervals the outer layer is removed, and extracted with water.

The term "saltpetre" is derived from the fact that this salt was and is still obtained from certain oily or feldspathic rocks by boiling the weathered rock with slaked lime and potash.

Saltpetre is used in the laboratory as a source of nitric acid for demonstration, as an oxidizing agent (substances are fused with KNO_3 for this purpose), and in preparing cooling mixtures.

QUERY. How are freezing mixtures prepared? Explain the philosophy of the process.

In domestic economy, it is used as a preservative of meat; but the most important purpose for which nitre is used is in manufacturing gunpowder.

Gunpowder consists of an intimate mixture of nitre, sulphur, and charcoal, in somewhat varying proportions. Sporting powder consists of nitre, 78.99, sulphur, 9.84, and charcoal, 11.17 parts. The explosive force of gunpowder depends upon the fact that it contains within itself the necessary amount of oxygen for its own combustion, whereby large volumes of heated gases (principally carbon dioxide and nitrogen) are liberated.

QUERY. What effect has the invention of gunpowder had on civilization? Give the philosophy of explosions in general.

(*h*) *Potassium Carbonate*, or *Potash*, K_2CO_3, is usually obtained from wood ashes. The ashes are lixiviated or "leached," and the lye thus obtained is evaporated till the solution is saturated, when impure crystals of the carbonate are deposited. These crystals are purified by roasting in a reverberatory furnace.

Other sources of potash are potassium sulphate, beet-root ashes, and *suint*.

Potassium carbonate is used in preparing other salts, as potassium cyanide, chromate, acetate, etc., and as a reagent.

An acid salt, $KHCO_3$, is prepared by passing a current of carbon dioxide gas through a solution of the normal carbonate.

(*i*) *Potassium Cyanide*, KCN or KCy, is an important compound, used in the laboratory as a reducing agent; also used in photography, and as a solvent for silver sulphide or oxide.

It is prepared by heating the ferro-cyanide with the carbonate to a red heat in iron crucibles, thus: —

$$K_4Fe(CN)_6 + K_2CO_3 = 5\ KCN + KCNO + CO_2 + Fe.$$

The chemically pure cyanide is prepared by passing hydrocyanic acid gas into an alcoholic solution of potassium hydroxide.

(*j*) There are other potassium salts in which the metal is combined with organic acids, and some of which are used in the laboratory.

The student will notice the tartrate, oxalate, and acetate.

360. Tests for Potassium.—1. Potassium compounds, on the platinum loop, color the Bunsen flame violet; but the presence of sodium obscures this test, hence it is necessary to observe the flame through thick cobalt-blue glass, which shuts off the sodium rays but transmits the potassium color.

NOTE. Always thoroughly clean the wire before testing.

2. The spectrum furnishes two easily distinguished lines,—K*α* in the extreme red, and K*β* in the violet.

3. Potassium salts, in concentrated solutions, and in the absence of all non-alkaline bases, yield, with tartaric acid, a white, distinctive precipitate, $KHC_4H_4O_6$, this is granular-crystalline, and may be tested further by 1.

SODIUM.

SYMBOL, NA'.—ATOMIC WEIGHT, 23.—SPECIFIC HEAT, 0.2394.
—MELTING-POINT, 95.6°.

361. Occurrence.—The chief and most plentiful sodium compound is common salt, sodium chloride, NaCl. Salt occurs in sea-water, most mineral waters, and drinking water, while traces of it are to be found in nearly all river waters. In some localities in the United States—as at Syracuse, N.Y., and the Saginaw Valley, Mich.—salt water or brine is found in vast reservoirs at a considerable depth below the surface of the earth. Wells are sunk in such localities, and the brine is raised to the surface by pumps, and utilized as a source of the salt used in commerce. Again, large beds of native salt or *rock salt* occur in various localities.

Another source of sodium is the native nitrate, $NaNO_3$, or Chili saltpetre, which occurs in beds in Chili and Peru.

A large tract of territory in the western United States is known as the Alkali Plains, owing to the occurrence of sodium compounds: the water and the very earth itself are saturated with alkali to such an extent that but scant vegetation grows, and, with the exception of one or two species of worms, the waters of the lakes, although clear as crystal, are uninhabited.

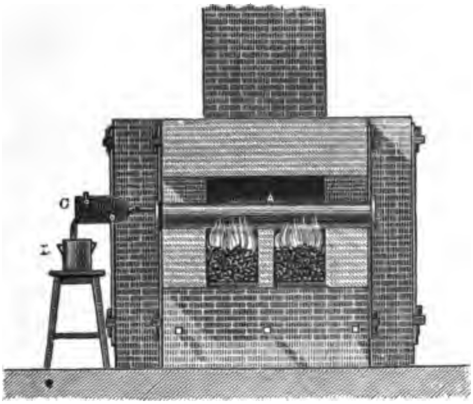

FIG. 20.

A is the iron tube retort coated with clay.
C is the condenser.
D is the cup containing rock oil.

In its distribution, sodium is the most persistent and universal of all the metals; indeed, it is nearly impossible to find a compound that will not yield the sodium test.

362. Preparation.—Sodium is prepared precisely like potassium, excepting that the carbonate and charcoal, instead of the tartrate, are employed. It is somewhat more easily obtained, however, and no explosive compound is formed.

Fig. 20 will give a good idea of the furnace employed in obtaining metallic sodium and potassium. After the condenser is filled with the metal, it is taken off and put under rock oil, after which the metal is scratched off.

363. Properties, Uses, and Compounds of Sodium. — Sodium is a light, silver-white metal which oxidizes readily in damp air.

It does not act upon water with as much violence as potassium, but it will take fire when thrown upon hot water, starch paste, or wet paper.

QUERIES. What purpose does the starch paste serve? Explain the phenomenon of sodium burning on hot water. What metals are obtained by the aid of metallic sodium?

SODIUM FORMS MANY USEFUL SALTS, OF WHICH WE NOTICE THE FOLLOWING: —

(*a*) *Sodium Hydroxide*, or *Caustic Soda*, NaOH, is prepared on the large scale by decomposing sodium carbonate with slaked lime, thus: —

$$Ca(OH)_2 + Na_2CO_3 = 2\ NaOH + CaCO_3.$$

The aqueous solution is then treated precisely in the same manner as caustic potash. Caustic soda is also prepared in large quantities from the red liquors from which the black crystals obtained in the soda-ash process are deposited.

QUERIES. When metallic sodium acts on water, is NaOH obtained? Try it. How can you decide what this substance is?

The principal use of caustic soda is in soap making. In the laboratory it is a useful reagent.

(*b*) *Sodium Chloride*, or *Common Salt*, NaCl, is obtained from various sources, as previously indicated. The strong brine of the salt wells is evaporated in shallow tanks by the aid of steam until the salt crystals are deposited. Salt is obtained from sea-water by allowing it to flow into large, shallow pans or vats called "salterns," where it is evaporated through the agency of the wind and sun.

SUG. Student mention the many uses of common salt.

(*c*) *Sodium Nitrate* or *Chili Saltpetre*, $NaNO_3$, occurs in vast deposits in Peru and Bolivia, and is now used as a source of nitric acid and as a fertilizer.

QUERIES. What other use of $NaNO_3$ was mentioned above under potassium? What element is obtained from Chili saltpetre?

(*d*) *Acid Sodium Hyposulphite*, $NaHSO_2$, is obtained by treating a solution of sodium hydrogen sulphite, $NaHSO_3$, with granulated zinc.

It is used by dyers and calico printers to reduce indigo, and in the laboratory for estimating free oxygen quantitatively.

(*e*) *Sodium Sulphate*, Na_2SO_4, with some admixture of the acid sulphate, $NaHSO_4$, is prepared in the first stage in the manufacture of soda or sodium carbonate. It is known as "salt-cake."

(*f*) *Sodium Thiosulphate*, $Na_2S_2O_3 + 5\ H_2O$, is used as an antichlor by paper manufacturers, and in the photographic process for dissolving out the unaltered silver salts. It is prepared by boiling caustic soda with sulphur, and then passing sulphur dioxide gas until the yellow solution obtained is decolorized. Its solvent action on silver salts is due to the formation of a double salt of sodium and silver, $NaAgS_2O_3$: —

$$Na_2S_2O_3 + AgCl = NaAgS_2O_3 + NaCl.$$

(*g*) *Sodium Hypophosphite*, NaH_2PO_2, is prepared by adding calcium hypophosphite to a solution of sodium carbonate. The filtered solution is then evaporated in vacuo. It is used in medicine.

(*h*) *Disodium Phosphate*, Na_2HPO_4, is used in medicine as a mild cathartic, and in the laboratory as a reagent. It is prepared by treating phosphoric acid with sodium carbonate.

(*i*) *Sodium Carbonate*, Na_2CO_3, is the chief product of soda-ash manufacture. Soda-ash is a mixture of the carbonate and hydroxide. The normal carbonate is used as an indispensable reagent in dry reactions in the laboratory.

The manufacture of soda-ash is a great industry by itself. The English process is thus described by Roscoe:—

"This substance, known in commerce as soda-ash, is manufactured in England on an enormous scale, and used for glass making, soap making, bleaching, and various other purposes in the arts. Formerly it was prepared from barilla or the ashes of sea-plants, but now it is wholly obtained from sea-salt by a series of chemical decompositions and processes, which may be divided into two stages:—

"1. Manufacture of sodium sulphate, or salt-cake, from sodium chloride (common salt); called *salt-cake process*.

"2. Manufacture of sodium carbonate, or soda-ash, from salt-cake; called *soda-ash process*.

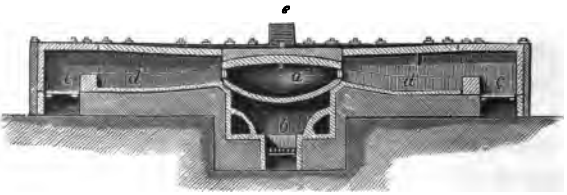

FIG. 21.

"1. *Salt-Cake Process.*—This process consists in the decomposition of salt by means of sulphuric acid. This is effected in a furnace called the Salt-Cake Furnace. Fig. 21 shows the section of such a furnace. This is drawn to a scale from one actually in use. It consists of (1) a large covered iron pan, *a*, placed in the centre of the furnace, and heated by fire placed underneath; and (2) two roasters or reverberatory furnaces, *dd*, placed one at each end, and on the hearths of which the salt is completely decomposed. The charge of half a ton of salt is first placed in the iron pan, and then the requisite quantity of sulphuric acid allowed to run in upon it. Hydrochloric acid gas is evolved, and escapes through a flue, *e*, with the products of combustion into towers or scrubbers filled with coke or bricks moistened with a stream of water. The whole of the acid vapors are thus condensed, and the smoke and heated air pass up the chimney. By recent act of Parliament, the alkali makers are compelled to condense at least 95 per cent of the hydrochloric acid gas they produce; and so perfectly is this condensation as a rule carried out, that the escaping gases do not cause a turbidity in a solution of silver nitrate, proving the absence of even a trace of the acid gas. After the mixture of salt and acid has been heated for some time in the iron pan, and has become solid, it is raked on to the hearths of the furnaces at each side of the decomposing pan, where the flame and heated air of the fire complete the decomposition into sodium sulphate and hydrochloric acid.

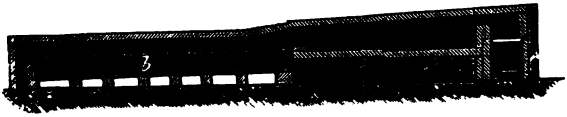

FIG. 22.

"2. *Soda-Ash Process.* — This process consists (1) in the preparation of sodium carbonate, and (2) in the separation and purification of the same. The first chemical change which the salt-cake undergoes in its passage to soda-ash is its reduction to sulphide, by heating it with powdered coal or slack: —

$$Na_2SO_4 + C_4 = Na_2S + 4\ CO.$$

The second decomposition is the conversion of the sodium sulphide into sodium carbonate, by heating it with chalk or limestone (calcium carbonate): —

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

These two reactions are in practice carried on at once, a mixture of ten parts of salt-cake, ten parts of limestone, and seven and a half parts of coal being heated in a reverberatory furnace called the Balling Furnace (shown in section in Fig. 22) until it fuses and the above decomposition is complete, when it is raked out into iron wheelbarrows to cool. This process is generally termed the black-ash process, from the color of the fused mass.

"The next operation consists in the separation of the sodium carbonate from the insoluble calcium sulphide and other impurities. This is easily accomplished by lixiviation, or dissolving the former salt out in water. On evaporating down the solution, for which the waste heat of the black-ash furnace is used, the heated air passes over an iron pan (see *b*, Fig. 22) containing the liquid. On calcining the residue, the soda-ash of commerce is obtained."

Ammonia Process. — Another process for converting sodium chloride into sodium carbonate is now used extensively. It consists in treating a solution of sodium chloride with ammonia and carbon dioxide: —

$$NaCl + NH_3 + H_2O + CO_2 = NaCl + NH_4HCO_3.$$

The acid ammonium carbonate acts upon the sodium chloride, forming acid sodium carbonate, $NaHCO_3$, which is difficultly soluble and is deposited: —

$$NaCl + NH_4HCO_3 = NH_4Cl + NaHCO_3.$$

The acid carbonate is heated and thus converted into the neutral salt: —

$$2\ NaHCO_3 = CO_2 + H_2O + Na_2CO_3;$$

and the carbon dioxide given off is used for the purpose of saturating the ammonia contained in the original solution. The ammonium chloride obtained in the second stage of the process is decomposed either by lime, CaO, or magnesia, MgO, and the ammonia thus recovered. This process is also known as the Solvay process, as its introduction is due to the exertions of M. Solvay.

Soda Crystals, or *Sal Sodae*, much used in softening hard water, are obtained by dissolving soda-ash in water, and allowing the crystals to deposit from a saturated solution. These crystals possess the formula $Na_2CO_3 + 10\ H_2O$.

Acid Sodium Carbonate, $NaHCO_3$, can be obtained from soda crystals by allowing them to be acted upon by CO_2 gas. This substance is known as Bicarbonate of Soda, and is employed in medicine and for preparing effervescing drinks. In domestic economy it is used as Saleratus and as an ingredient of Baking Powder.

(*j*) *Silicates.* Glass is a silicate of calcium and either sodium or potassium. Ordinary glass contains sodium. The difficultly fusible Bohemian glass contains potassium. For some purposes, lead is introduced instead of calcium. Glass made in this way, having a high refractive power, is very useful for optical purposes. Ordinary glass is made by melting together quartz and quicklime or calcium carbonate and sodium carbonate.

(*k*) Many other salts of sodium may be obtained in the shops, and are very useful in preparing test solutions, especially when the student is working for acids in the non-metals.

364. Tests for Sodium.—1. Sodium compounds color the non-luminous flame intensely yellow, and this color is obscured by the blue glass.

NOTE. Any substance, as dirt on the platinum wire, will give this test for sodium. Therefore, clean the wire carefully, and convince yourself that the color is not caused by the ordinary impurities. Try some known sodium compound till you recognize the flame.

2. The sodium spectrum gives two intense lines in the yellow which lie so close that they often seem but one. They coincide with Fraunhofer's D lines in the solar spectrum.

AMMONIUM.

SYMBOL, NH_4. — MOLECULAR WEIGHT, 18.

365. When sodium amalgam containing one to three per cent of sodium is thrown into a strong solution of ammonium chloride, a curious spongy substance is formed, which gradually rises in the vessel, filling a large amount of space. It is very unstable, giving off ammonia and hydrogen, and leaving metallic mercury. This substance, according to the most careful examinations, contains nitrogen and hydrogen in the proportions indicated in the formula NH_4, and this is simply in combination with mercury. As this group plays the part of a metal in the salts obtained from ammonia and the acids, — as in $(NH_4)Cl$, $(NH_4)NO_3$, $(NH_4)_2SO_4$, etc., — it is called *ammonium*, and the compound with mercury, *ammonium amalgam;* hence, further, the salts obtained with ammonia are called ammonium salts. The metal ammonium, NH_4, is, however, hypothetical.

OF THE AMMONIUM SALTS WE NOTICE: —

(*a*) *Ammonium Chloride*, or *Sal Ammoniac*, NH_4Cl, which occurs as a natural deposit, but is now prepared from the ammoniacal liquors of gas works. The ammonia gas is liberated from the gas liquors by adding slaked lime, and is led into a dilute solution of hydrochloric acid, from which this salt is obtained by evaporation; the chloride is afterwards purified by sublimation. This salt is used as a reagent and as a source of ammonia in the laboratory, and as an important aid in soldering, welding, etc.

(*b*) *Ammonium Nitrate,* NH_4NO_3, is used as a source of Laughing Gas or Nitrous Oxide, and can be prepared by neutralizing nitric acid with ammonia.

(c) *Sodium-Ammonium Phosphate*, or *Microcosmic Salt*, $HNaNH_4PO_4 + 4\ H_2O$, is much used in blow-pipe work, since it forms a colorless bead on the platinum wire, and receives a color by adding certain substances. It is formed by the decomposition of urine, and is artificially prepared by dissolving five parts of sodium phosphate with two parts of ammonium phosphate in hot water, and allowing the solution to cool.

(*d*) *Ammonium Carbonate*, $(NH_4)_2CO_3$, is used as a group reagent, and is now prepared by subliming $CaCO_3$ with ammonium sulphate, and digesting the product formed with strong aqua ammoniae.

(*e*) *Ammonium Sulphide*, $(NH_4)_2S$, is used as a group reagent, and is very unstable, passing into $(NH_4)_2Sx$ upon exposure. This reagent is readily prepared in the laboratory when needed by passing a current of hydrogen sulphide gas into aqua ammoniae until the solution will not precipitate magnesium sulphate.

366. Tests for Ammonium. — The tests for ammonium have already been given (Art. 55), and it only remains to add that, in the course of analysis, although the ammonium salts remain in the fifth group, it is necessary to apply these tests directly to the original solution.

THE RARER METALS OF THE FIFTH GROUP.

LITHIUM.

SYMBOL, Li'. — ATOMIC WEIGHT, 7.

367. Lithium is a rare metal which is found in Lepidolite, Triphylline, $(Li, Na)_3PO_4 + (Fe, Mn)_3PO_4$, and some other minerals. This metal occurs in most surface waters and in many mineral waters, and easily finds its way into the animal and vegetable kingdoms.

It is prepared by electrolyzing its chloride, and is a silver-white metal, readily oxidizing in the air.

The principal salt is the carbonate, which is used in medicine. The chloride, nitrate, sulphate, etc., can be prepared by treating the carbonate with the proper acid.

QUERY. Why are the carbonates of the metals chiefly employed in preparing the rarer salts?

368. **Tests for Lithium.** — 1. Lithium compounds color the flame intensely crimson; this color is obscured only by very thick blue glass.

2. The spectrum of lithium affords a certain test, yielding the bright-red line, Liα, and the weak yellow line, Liβ.

RUBIDIUM.

SYMBOL, RB′. — ATOMIC WEIGHT, 85.

369. Rubidium is prepared like potassium, which metal it closely resembles. It is widely distributed, but occurs only in very minute quantities. It is found in Lepidolite, Triphylline, Mica, Orthoclase, and other minerals, as well as in various waters and soils.

Rubidium is detected by its coloring the flame somewhat more red than potassium, but more certainly by its spectrum, which yields two violet lines, Rbα and Rbβ.

CÆSIUM.

SYMBOL, Cs′. — ATOMIC WEIGHT, 133.

370. Cæsium is the first metal discovered by the spectroscope, and occurs with the other alkali metals. It has not been prepared, but its salts are known.

Cæsium is detected by its spectrum, which yields the bright-blue lines, Csα and Csβ.

371. Detection of the Fifth Group Metals. — 1. Test the original solution for ammonium.

2. Free the solution from the first four groups (magnesium excepted) by adding NH_3, NH_4Cl, and $(NH_4)_2CO_3$; the filtrate is to be tested for Na, K, and Li; accordingly, evaporate the solution nearly to dryness, and proceed thus: —

(*a*) The sodium flame is to be observed by the naked eye, and is intensely yellow.

NOTE. Remember that traces of sodium are usually present.

(*b*) Sodium obscures the violet potassium flame, but the potassium flame becomes visible when observed through the blue glass which shuts off the sodium color.

(*c*) The lithium flame is readily determined by its crimson color. It is obscured only by very thick blue glass. The lithium flame is visible even when Na and K are present.

GENERAL NOTE. The student is not to infer that the analytical grouping of the metals or the numbering of the groups is otherwise than purely arbitrary. Many different groupings can be made, depending upon the reagents employed in the course of analysis. The following table will enable the student to compare the grouping and numbering used in this book with those used by Fresenius: —

I.	K, Na, NH_4, Li	V.
II.	Ba, Sr, Ca, Mg	IV.
III.	Al, Cr	III.
IV.	Zn, Mn, Ni, Co, Fe	
V.	Ag, Hg, Pb	I.
	Bi, Cu, Cd	II.
VI.	As, Sb, Sn	

The Roman numerals in the first column indicate the groups given in Fresenius.

372. To Analyze an Unknown Solution. — In making a complete qualitative analysis of an unknown solution, it is desirable to proceed by a methodical plan. From what has preceded, it is evident that the first step should be to determine the bases; this may be accomplished as indicated in the following table. When we know what bases are present, we are then prepared to determine the acids. In case we obtain arsenic, chromium, manganese, etc., we know that these elements are apt to be present as acids. Accordingly we first try for the acids formed by those elements. In case these elements are not present, we remove the bases by E (as explained farther on), *and then test for acids* as in Art. 227.

A.

The solution may contain a salt of:—

$$\begin{array}{r|l|} \hline 1. & \text{Pb, Ag, or Hg}' \\ \hline 2. & \text{Hg, Cd, Pb, Cu,} \\ & \text{Bi, As, Sb, Sn} \\ \hline 3. & \text{Fe, Cr, Al, Zn,} \\ & \text{Mn, Ni, Co....} \\ \hline 4. & \text{Ba, Sr, Ca, Mg} \\ \hline 5. & \text{K, Na, NH}_4\text{, Li} \\ \hline \end{array}\left.\vphantom{\begin{array}{l}1\\2\\3\\4\\5\\6\\7\end{array}}\right\} + \text{HCl} = \overbrace{\frac{\text{PbCl}_2}{\text{white}}, \frac{\text{AgCl}}{\text{white}}, \frac{\text{Hg}_2\text{Cl}_2}{\text{white}}}^{\text{The precipitates:—}} + \left\{\begin{array}{l}\text{Solutions of 2, 3, 4,} \\ \text{and 5.}\end{array}\right.$$

Filter out the precipitate, and proceed by Art. 247.
Treat the filtrate by B.

B.

Filtrate from A:—

$$\begin{array}{r|l|} \hline 2. & \text{Hg, Cd, Pb, Cu,} \\ & \text{Bi, As, Sb, Sn} \\ \hline 3. & \text{Fe, Cr, Al, Zn,} \\ & \text{Mn, Ni, Co....} \\ \hline 4. & \text{Ba, Sr, Ca, Mg} \\ \hline 5. & \text{Na, K, NH}_4\text{, Li} \\ \hline \end{array}\left.\vphantom{\begin{array}{l}1\\2\\3\\4\\5\\6\end{array}}\right\} + \text{H}_2\text{S} = \overbrace{\left\{\begin{array}{l} \frac{\text{As}_2\text{S}_3}{\text{yellow}}, \frac{\text{Sb}_2\text{S}_3,\ \text{Sb}_2\text{S}_5}{\text{orange}}, \frac{\text{SnS}}{\text{brown}}, \frac{\text{SnS}_2}{\text{yellow}}, \frac{\text{PbS}}{\text{black}}, \\ \frac{\text{Bi}_2\text{S}_3}{\text{black}}, \frac{\text{CuS}}{\text{black}}, \frac{\text{CdS}}{\text{yellow}}, \frac{\text{HgS}}{\text{black}} + \left\{\begin{array}{l}\text{Solutions of} \\ \text{3, 4, and 5.}\end{array}\right. \end{array}\right.}^{\text{The precipitates:—}}$$

Filter out the precipitate, and proceed by Art. 278.

Boil the filtrate to expel H_2S, and add a little HNO_3, and boil a short time to oxidize ferrous to ferric salts, and then proceed by C.

C.

Filtrate from B: — The precipitates: —

$$\left.\begin{array}{r|l|} \cline{2-2} 3. & \text{Fe, Cr, Al, Zn,} \\ & \text{Mn, Ni, Co....} \\ \cline{2-2} 4. & \text{Ba, Sr, Ca, Mg} \\ \cline{2-2} 5. & \text{Na, K, NH}_4\text{, Li} \\ \cline{2-2} \end{array}\right\} \begin{array}{l} + NH_3 + NH_4Cl = \overbrace{\frac{Fe_2(OH)_6}{\text{reddish brown}}, \frac{Cr_2(OH)_6}{\text{bluish green}}, \frac{Al_2(OH)_6}{\text{white gelatinous}}} + \\ \quad \text{Solutions of Zn, Mn, Ni, Co, 4, and 5.} \\ \textit{Filter out these precipitates, and proceed by Art. 303.} \\ (\text{To the filtrate}) + (NH_4)_2S = \frac{MnS}{\text{flesh col.}}, \frac{CoS}{\text{black}}, \frac{NiS}{\text{black}}, \frac{ZnS}{\text{white}} + \\ \quad \text{Solutions containing 4 and 5.} \end{array}$$

Filter out this precipitate, and proceed by Art. 321.

Boil the filtrate to expel H_2S, and proceed by D.

D.

Filtrate from C: — The precipitates: —

$$\left.\begin{array}{r|l|} \cline{2-2} 4. & \text{Ba, Sr, Ca, Mg} \\ \cline{2-2} 5. & \text{Na, K, NH}_4\text{, Li} \\ \cline{2-2} \end{array}\right\} + NH_3 + NH_4Cl + (NH_4)_2CO_3 = \overbrace{\frac{BaCO_3}{\text{white}}, \frac{SrCO_3}{\text{white}}, \frac{CaCO_3}{\text{white}}} + \text{Mg and 5.}$$

Filter out these precipitates, and proceed by Art. 355.

Divide the filtrate in two parts; to one of these parts add Na_2HPO_4: precipitate, $\frac{MgNH_4PO_4}{\text{white}}$.

Test the second part by Art. 371 for 5.

Test for acids by E.

E.

1. If the solution contains arsenic, chromium, or manganese, etc., test the solution for the acids formed by these elements.

2. When the solution contains only the metals of the fifth group, test the original solution directly for acids, following the directions under Art. 227, and as given under each acid in the non-metals.

3. When other metals, not acid forming, are found, it is best to make the solution neutral with KOH, and then to add K_2CO_3 to precipitate them. Filter out the precipitate, and test the filtrate. In case calcium superphosphate be present, the phosphate will be found in the precipitate.

Now, since we have added a carbonate, the filtrate contains the added carbonate. In consequence of this, we must test the original solution for carbonates. Before proceeding as in Art. 227, it is best to remove the added carbonate by means of HCl; in this way we get a solution which may be tested for all the non-metallic acids excepting HCl. We may prepare another portion of the filtrate containing the added carbonate by adding HNO_3; this solution is to be tested for HCl.

Test for some Organic Acids given under F.

F.

1. *Tartaric Acid*, $H_2(C_4H_4O_6)$, is detected by adding $AgNO_3$ to the normal solution; a white precipitate is thrown down, which turns black on boiling. And further, when tartaric acid is ignited, it gives off the odor of burnt sugar. $CaCl_2$ gives a white precipitate, $Ca(C_4H_4O_6)$, soluble in cold solution of KOH.

2. *Acetic Acid*, $H(C_2H_3O_2)$, forms a red solution with Fe_2Cl_6, which is not decolored by adding $HgCl_2$, while red KCyS solutions with Fe_2Cl_6 are thus decolored.

Also, when warmed with sulphuric acid and a little alcohol, acetic acid gives off the odor of acetic ether.

3. *Citric Acid*, $H_3(C_6H_5O_7)$, gives a white precipitate with $AgNO_3$, which does not blacken on boiling; also it gives a white precipitate with lead acetate. Further, concentrated nitric acid produces from it acetic and oxalic acids.

4. *Oxalic Acid*, $H_2C_2O_4$, is decomposed into CO_2 and CO by H_2SO_4.

When treated with $CaCl_2$, the oxalates give a white precipitate, soluble in HCl, insoluble in acetic acid. (See Art. 227.)

APPENDIX.

APPENDIX.

THE LABORATORY.

1. The Room selected for the chemical laboratory should be dry, well lighted, and well ventilated. Generally an upper room is preferable to a basement; basements are apt to be damp, and poorly lighted, and the laboratory fumes are not so easily restrained from diffusing themselves through the building; with proper precautions, however, little or no inconvenience will arise from the use of a dry, well ventilated basement room.

It is desirable that the rooms devoted to chemistry and physics should be adjacent to each other, as many pieces of apparatus will illustrate portions of both studies. If communication between the two rooms can be secured by sliding doors, so much the better; this arrangement offers many advantages in those schools where chemistry and physics are taught by the same teacher. In case the rooms cannot be adjacent, they should be as near together as possible.

GENERAL FIXTURES.

In case the building is heated by steam, and lighted by gas, many of the general fixtures are easily provided.

2. The Condenser for procuring distilled water may be connected directly to the steam-pipes used in heating the building. A plain sheet copper cylinder 30^{cm} in diameter, and 135^{cm} high, will afford all the distilled water thirty students will require: this cylinder simply needs a faucet at the bottom, through which the water may be drawn when needed, and a small pet-cock at the top, through which the air is to be blown out when the steam is first turned on. The steam is admitted at the top of the cylinder which stands upright, and which needs no internal coil nor external jacket. The cylinder should be able to carry all the pressure that the boilers are likely to put upon it, and it may stand in any convenient part of the room, as no hissing or other disagreeable noise is heard.

In case the building does not contain steam, permission may be obtained from some factory or mill to connect such a condenser to the boilers used there. The connecting pipe should be as small as possible, and the steam should be allowed merely to leak through the valve, by means of which the condenser is shut off from the boiler.

Many other devices are to be had, some of which are applicable under one condition, while under other conditions another device may succeed more satisfactorily, *e.g.*

Small quantities of distilled water are to be had by means of a Liebig condenser, in connection with a still heated by a gasoline stove, or by an ordinary stove; a coil may be passed through a cask containing cold water, etc., etc.

One fact should be noted here; ordinary rain-water, and water as usually prepared by distillation, usually contain free ammonia. Water free from ammonia may be obtained as explained in App. 77.

3. **The Tank for Wash-Water** may be placed in a corner of the room, and its bottom should be four or five feet higher than the faucets from which the water is drawn. Pipes leading from the tank may carry the water to a sink and to each student's desk.

Pure cistern water is best for ordinary washing purposes in a laboratory; the water may be raised to the tank by a force-pump, or a cistern may be constructed under the roof of the building.

4. **A Gas Chamber** is useful for many purposes. It may be built of sash with glass, and it may stand in any convenient place, so that it may be connected to a good ventilating shaft. By means of such an arrangement, the operator can observe what is taking place, and the unwholesome gases generated are carried out of the building. It is convenient to have two or three separate apartments not in communication with one another, and each one with a separate door. The size of such a chamber will depend upon the requirements of the school, but one 3 ft. square × 6 ft. high will answer for most small laboratories.

5. **Cases** for chemicals, apparatus, etc., are convenient and inexpensive. It is desirable to have a portion of the case provided with sash doors, and the remainder is to be cased with panel doors, thus providing dark closets in which stock chemicals and reagents may be kept to better advantage.

6. **Working Tables** may be placed against the walls of the room, or through its centre. A table 15 ft. long, 3 ft. 1 in. high, and 3 ft. 4 in. wide, and standing from the walls, will afford ample room for eight

students to work at a time. If the class be divided into two working divisions, such a table will accommodate sixteen students, while the apparatus per student will thereby be materially lessened. In the centre of the table are placed four desks, while sink-bowls are placed between. One side of such a desk is shown in the Frontispiece; this cut is taken from the photograph of a desk in Ypsilanti High School Laboratory. In the table just under the desk is a drawer, used by the student to keep his apron and other personal property which he requires in his work.

The tables may be supported by legs or by square posts; in the latter case, cupboards may be constructed under the tables; but in case cupboards are made, a bottom or an extra floor should be put in, so that the base-board under the doors may not form an obstruction in sweeping out any dust, etc., that may collect in the cupboard.

The dimensions of the desk shown are as follows: Height, 2 ft. 4 in.; length, 2 ft. 6 in.; breadth at bottom, 14 in.; at top, 12 in.; space underneath first shelf, 11 in.; second space, 8 in., and third space 6 in. The top of the desk may be utilized as a shelf. A partition through the desk divides it into halves, thus forming two working cupboards, one on each side of the desk.

The gas chamber, tables, desks, and cases, can be made by any carpenter.

APPARATUS AND REAGENTS.

In considering the materials under this heading, it will be convenient to follow the order: —

(*a*) Apparatus for the student's desk;
(*b*) Reagents for the student's desk;
(*c*) Reagents for the side table;
(*d*) Working material;
(*e*) General apparatus for the laboratory.

APPARATUS FOR THE STUDENT'S DESK.

Perishable apparatus, such as glass and porcelain ware, should be kept in stock in order to supply quickly any loss by breakage, etc.

7. **Test-Tubes.** — At the start the student should have twelve 4-in. test-tubes, and two 8-in. test-tubes of a larger diameter. The latter are to be fitted with rubber stoppers pierced with one hole, through which is inserted a bent delivery-tube; they are used as generators.

Test-tubes are perishable, but they are not expensive. A liquid may be heated in a test-tube by placing the tube directly in the Bunsen or alcohol flame, provided the flame does not strike the tube at the upper level of the liquid.

When heating a substance in a test-tube, *the student should never hold the mouth of the tube towards himself nor towards others*, since any explosion, as of steam or other gases, might result seriously; it is best to move the test-tube gently through the flame when heating any substance.

With a little practice the student may mend a test-tube, the bottom of which has been broken. To accomplish this, the tube is first to be cleaned and dried; the broken end is then strongly heated in the Bunsen flame until the glass becomes soft; the broken edges of the tube are now forced together by means of a bit of glass tubing; when the bottom is closed, the end of the tube is freed from unnecessary material by carefully drawing out the highly heated end of the tube with the glass rod; the end of the tube is now strongly heated until it becomes somewhat thicker than the walls of the tube; now the mending is to be finished by blowing gently into the tube, in order to give the end a rounded form. When heating the tube, it should be rolled over constantly in the flame, so that all sides may be heated alike. An alcohol or gas blast-lamp may be used to good advantage for this work, and for such other glass-work as usually must be done in the laboratory.

8. **Hard Glass Tubing.** — Each student should have a tube 8 in. long, and with a bore of about ¼ in.; this is used for heating solids as in Exp. 3 P.

A hard glass test-tube has been mentioned in the text. These are more expensive than ordinary test-tubes; for most purposes mentioned a common tube may be used, but it is almost invariably ruined; this is of no great moment, however, if a tube that has been mended is employed.

9. **A Test-Tube Rack** for holding test-tubes is shown in the Frontispiece. The student can make this for himself by taking a suitable block of wood and setting in one edge of it a row of wooden pins 3 in. high; in the other edge holes are bored, which will serve to hold tubes containing liquids.

10. **A Test-Tube Swab** for washing out test-tubes is also to be made by the student. It is simply a wooden stick as large as a lead-pencil, upon the end of which a bit of sponge is fastened.

Test-tube brushes of various designs are also to be had in the market, but the swab will answer for nearly every purpose.

11. **A Glass Stirring-Rod** may be made from suitable solid glass rods

which are to be kept in the laboratory. This rod should be about as large and long as a common slate-pencil. The ends of the rod must be melted smooth and round in the Bunsen flame.

12. **Platinum Wire and Platinum Foil** are much used. The wire should be about 3 in. long, and one end of the wire should be fused into a short glass tube; the other end of the tube should be closed. The platinum foil may be about 1 in. × ½ in. The uses of these articles are described in the text in the appropriate places.

13. **A Blow-Pipe** of the form shown in the Frontispiece (BP), known as Black's, is the best of the cheaper forms. A blow-pipe should last many years.

14. **Steel Tongs** (T in Frontispiece) are useful to handle hot evaporating dishes, hot crucibles, etc. The student may readily hold a test-tube while boiling solutions, etc., by putting a narrow strip of cloth around the upper end of the tube and clasping the ends of the strip in these tongs. These tongs should last five or six years.

15. **Funnels** are shown in FN; these are of glass. The student should have two, — one 2 in. and one 3 in. or 4 in. in diameter. The funnels should have their stems ground off at an acute angle to facilitate the process of filtration. Funnels are seldom broken.

16. **Filter-Papers** should be cut round, and should be furnished the student in packages. The proper size papers for the funnels are 4 in. and 6 in. in diameter. These papers should be kept in a tin box of prope. form and size.

The filter-papers are placed in the funnel as follows: First, they are folded through the centre; then another fold, at right angles to the first, is made, which leaves the paper in the form of a sector of a circle; now, by inserting the apex of the sector into the funnel, the paper may be opened out in form of a cone that will fit the funnel. It will be seen that two pockets are formed in the paper, either of which will serve as a receptacle for the fluid to be filtered. It is best to wet the paper with distilled water before filtering a solution containing a precipitate, as this tends to prevent the precipitate from adhering so closely to the paper.

Beginners are often at a loss as to how they may divide small precipitates into several parts; this may be accomplished in different ways, of which these two are as convenient as any: First, the point of the filter-paper containing the well-washed precipitate may be pierced, and the damp precipitate may be washed through into a beaker glass by means of distilled water; the precipitate may now be agitated with a stirring-rod until it is suspended in the water, when portions of it may be poured out; Second, the precipitate may be left on the filter-paper, and whether damp or dry may be separated into portions by tearing the filter-paper into the requisite number of parts. If the precipitate be damp, it may be washed off each part as needed, by means of water. If the precipitate be dry, and the student wishes to dissolve the dried precipitate, he may put the paper and all in a test-tube, and after dissolving may remove the particles of the filter-paper by passing the solution through a new filter.

For filtering acids a little spun glass is best; this may be crowded down into the stem of the funnel, and after passing the acid through it may be washed and preserved for further use.

17. Generating Flasks, one each of 2-oz. and 4-oz. capacity, will answer for the student's needs. These flasks are used for generating gases, etc., and are fitted with delivery-tubes as shown in the Frontispiece, F. These flasks are sometimes broken.

18. Two Beaker Glasses (see Bk in Frontispiece), one of 2-oz. and the other of 4-oz. capacity, are needed. In them solutions are boiled, crystals are allowed to form, and solutions for working purposes are kept temporarily, etc., etc. Neither these beakers nor the Florence flasks mentioned in 17 should be heated in the naked Bunsen flame. They should always be placed on wire gauze or on a sand-bath.

19. Evaporating Dishes (see E in Frontispiece), one each of about 3-oz. and 4-oz. capacity, are needed. These should be heated on the sand-bath or on wire gauze. They are seldom broken. Prof. Weitbrecht's students frequently use saucers as evaporating dishes.

20. A Bunsen Burner is shown at B. The use of this has been explained. In laboratories not containing gas for heating purposes, alcohol lamps are the best substitute. In nearly every place in the text where "Bunsen flame" has been used, "alcohol flame" may be substituted.

21. A Wash-Bottle, or "**Blow-Bottle**" as it is familiarly termed by students, is shown at W in Frontispiece, as made by a student from whose desk this cut was taken. Each student can make his own bottle; the delivery-tube should be drawn out into quite a fine jet, so that the stream of water issuing from it, upon blowing into the mouth-piece, shall be quite small.

22. Each Student should provide himself with a toy magnet, a clay tobacco pipe for blowing soap-bubbles, a sponge, a towel, a bundle of soft white rags, a box of matches, a watch-crystal, an oil-cloth apron, and a pair of rubber sleeves. The uses of these are too evident to need mentioning.

23. **A Ring Stand** is shown at A. This is used to support funnels while filtering, and sand-baths, retorts, generating flasks, etc., while heating. The rings may be removed or clamped in any position upon the upright standard.

24. **A Blue-Glass** is shown at G. This is a frame containing two thicknesses of glass. One blue-glass will answer for two desks.

25. **A Sand-Bath** is shown at S, resting on a ring. This is a saucer-shaped sheet-iron dish, which may be hammered out by any tinsmith. It must be large enough to rest on the largest ring. The dish is filled with clean white sand, and in this sand beakers, evaporating dishes, etc., are set; the heat is applied to the sand-bath. There is one objection to a sand-bath, — the sand is apt to get scattered on the student's desk and find its way into the waste pipes leading from the sink-bowls. It is safer, however, to heat glass ware, etc., in a sand-bath than it is on a

Wire Gauze. This gauze is of fine brass wire, and is placed between the flame and the evaporating dish. It will be found to be neater and less objectionable in several respects than the sand-bath, but it is not quite so safe to heat fragile ware upon it.

Professor Foote recommends asbestos paper in place of the sand-bath and wire gauze.

26. **A Match-Safe** should be furnished to each desk, and the student should not be allowed to put matches in his drawer. Employ sulphur matches; parlor matches are too dangerous.

27. If the student is to do a little quantitative work, he will need, in addition to the foregoing, a porcelain crucible with cover, a feather, a sheet of glazed paper, and a triangle made by joining three common clay tobacco-pipe stems by means of iron wire.

28. **Litmus Papers.** These papers may be purchased ready for use, or they may be prepared in the laboratory by dipping sheets of bibulous paper in litmus solution; the papers thus prepared are blue. Red and blue papers are needed; the red papers may be prepared by moistening the blue papers in dilute acetic acid. The papers should be cut into strips 4^{cm} long and 4^{mm} wide; they may be kept in a bottle or cardboard box.

29. **Charcoal.** A fine variety of charcoal is to be purchased of chemical dealers, but selected pieces may be obtained from ordinary charcoal that will answer all purposes. Charcoal should not be kept in the drawers or on the desk. Separate pans with legs should be provided to avoid danger from fires.

The reagents for the student's desk should be kept in stock in the laboratory, *i.e.*, a sufficient quantity of the dry salts and of the liquid reagents should be purchased at the beginning of the year to last throughout that year. Some of these reagents are more convenient in a dry form; but most of these are used in the form of solutions.

The solutions should be kept in good glass-stoppered bottles, holding $\frac{1}{8}^{1}$ or 4 oz., similar to those shown in the Frontispiece. It is desirable that these bottles have permanent acid-proof names and symbols.

The dry salts should be kept in small 2-oz. salt-mouth bottles, and these are best when provided with glass stoppers.

A few words of caution concerning the care of reagent bottles are in place here. A good reagent bottle must have its stopper ground to fit it, and this stopper will not fit any other bottle in the set. Consequently the stoppers should never be interchanged. Again, the stoppers of all reagent bottles, excepting sulphuric acid, should be paraffined with gum-stock paraffin, otherwise they are quite apt to stick; often the bottles are ruined or cracked by trying to remove the stoppers. There is no excuse for breaking a reagent bottle. The solutions should not be allowed to freeze, as the bottles may thus be broken.

The student should not lay down the cork of a reagent bottle while pouring out a solution, since he may thus change stoppers with his bottles or contaminate his reagents. Again, no solution but the one corresponding to the name on the bottle should ever be placed in a reagent bottle.

Another important item is that each bottle have a place on its shelf, and always be put in its place; thus the student comes to know where to find a reagent, just as a printer knows where to find the letters in his case.

Since some order must be followed, that in which the reagents are described below may be insisted on. Commencing with the first name in the list on the upper shelf, left-hand side, arrange the bottles toward the right; and, when the shelf is full, begin again on the left-hand of the next.

Since systems of nomenclature vary somewhat, and since labels and names are apt to vary decidedly, all the names are given in connection with each reagent, the most preferable coming first, the symbol next, and thereafter the various other names, in order of their preference, excepting the name given in italics, which is that of the United States Pharmacopœia; its position has no reference to its preferment.

In naming the acids, the common names are given first, for the reason that these names are good ones, and in spite of all attempts to do away with them, they still persist in remaining; and it is perhaps but wise to submit to the inevitable. Thus, that acid whose formula is H_2SO_4, is called *sulphuric acid; hydrogen sulphate*, for some reasons, would be better, but the change is not universally accepted. Again, *hydric sulphate* has been proposed, but this is still less favorably received; while the oldest name of all, *oil of vitriol*, is scarcely used or known by the last generation of chemists, though still retained by manufacturers.

The reagents enumerated below (with a few exceptions, which are noted) should be chemically pure. Of all persons, a beginner should have the best materials to work with; moreover, good material is now so cheap that there is neither profit nor sense in using goods of a poor quality.

LIQUID REAGENTS.

30. Sulphuric Acid, H_2SO_4; Hydrogen Sulphate; Hydric Sulphate; Dihydric Sulphate; Oil of Vitriol; *Acidum Sulphuricum.*

This acid should be bought in a concentrated form, sp. grav. 1.843, and should be dealt out to students in this form; it should evaporate on platinum foil without leaving any residue, and it should be colorless.

The commercial acid may be contaminated with arsenic, antimony, iron, aluminum, calcium, potassium, sodium, lead, magnesium, hydrochloric acid, nitrous acid, nitric acid.

31. Nitric Acid, HNO_3; Hydrogen Nitrate; Hydric Nitrate; Aqua Fortis; *Acidum Nitricum.*

This acid may be bought in a concentrated form, and afterward reduced with water to reagent strength, which is 32 per cent acid, sp. grav. 1.32. (See 34 for computation.)

Pure nitric acid is colorless, but, on standing exposed to the light, it may become colored by the lower oxides of nitrogen, which, as a usual thing, are not harmful. They may be removed by passing a current of air through the acid by means of a glass tube attached to a hand-bellows.

The commercial acid may contain calcium, sodium, iron, oxides of nitrogen, hydrochloric acid, sulphuric acid.

32. Hydrochloric Acid, HCl; Hydrogen Chloride; Hydric Chloride; Muriatic Acid; Chlorhydric Acid; Chlorhydrate; Spirit of Salt; *Acidum Hydrochloricum.*

This acid may likewise be purchased in a concentrated form, and afterwards reduced to the reagent strength, 24 per cent acid, sp. grav. 1.12. The pure acid is colorless, and leaves no residue upon evaporation; upon standing, it may become colored by free chlorine.

The commercial acid may contain iron, sodium, aluminum, arsenic, sulphuric acid, sulphurous acid.

33. Acetic Acid, $H(C_2H_3O_2)$; Hydrogen Acetate; Hydric Acetate; *Acidum Aceticum.*

Since acetic acid is not so extensively used as the preceding acids, it may be purchased of a reagent strength, 30 per cent acid, sp. grav. 1.04. The pure acid is colorless, and leaves no residue upon evaporation.

The commercial acid may contain sodium chloride, lead, copper, iron, empyreumatic substances, sulphuric acid, sulphurous acid, nitric acid.

34. Ammonia, NH_3. The reagent solution contains 10 per cent of the gas NH_3, and has a sp. grav. 0.96. It is prepared from the "Stronger Water of Ammonia," or *Aqua Ammonia* (28 per cent gas; sp. grav. 0.90; U. S. P.), by the addition of distilled water. The concentrated form is more convenient to keep in stock, as it requires less space for storage. In the case of ammonia, and of the concentrated acids previously mentioned, the label of the original package should state the per cent and sp. grav.

Commercial aqua ammonia may contain ammonium chloride, ammonium carbonate, calcium sulphate, empyreumatic material.

The amount of water to be added to a given volume of a stronger solution may be determined by calculation. Thus, in the case of ammonia: We know that 1^l of the strong solution weighs 900^g, and that 28 per cent of that weight, or 252^g, is NH_3. It is evident that this 252^g is to form 10 per cent of the weight of the reagent solution; hence, the whole weight of the reagent solution will be $252 \div .1 = 2520^g$. Now, we already have taken 900^g of the strong solution; consequently $2520 - 900 = 1620^g$, or the weight of distilled water to be added to 1^l or 1000^{cc} of the strong solution. It is further evident that one part, by volume, of the strong solution requires 1.62 parts, by volume, of distilled water.

35. Ammonium Carbonate, $(NH_4)_2CO_3$; Carbonate of Ammonia; Ammonic Carbonate; Volatile Salt; *Ammonii Carbonas.*

This solution is prepared by dissolving 1 part by weight of the dry salt in 4 parts by weight of water, after which one part of reagent ammonia solution is added.

The commercial salt may contain calcium, iron, lead, chlorides, iodides, sulphates.

It is not necessary to weigh the water, since 1^{cc} of water weighs 1^g. The graduated ware used in measuring solutions is graduated at a certain temperature, usually 15° C. When accuracy is required, the temperature of the water or of the solution to be measured should be that at which the apparatus is graduated.

36. Ammonium Sulphide, $(NH_4)_2S$; Sulphide of Ammonium; Ammonic Sulphide.

This solution may be purchased ready for use, or it may be prepared in the laboratory by passing hydrogen sulphide gas through a reagent solution of ammonia until the solution no longer precipitates magnesium sulphate. This reagent changes, upon standing, to the yellow variety. Although the formula of the yellow ammonium sulphide has been given as $(NH_4)_2S_2$, its composition varies greatly.

37. **Ammonium Chloride,** NH_4Cl; Chloride of Ammonium; Ammonic Chloride; Muriate of Ammonia; Sal Ammoniac; *Ammonii Chloridum.*

To prepare this reagent solution, dissolve 1 part of the crystallized salt in 8 parts of water.

The commercial salt may contain iron, sulphates, organic matter.

38. **Ammonium Oxalate,** $(NH_4)_2C_2O_4$; Oxalate of Ammonium; Ammonic Oxalate.

This is prepared by dissolving the crystallized salt, $(NH_4)_2C_2O_4 + H_2O$, in 24 parts of water.

The commercial salt may contain sodium, potassium, calcium, aluminum, lead, sulphates, nitrates.

39. **Potassium Hydroxide,** KOH; Potassium Hydrate; Potassic Hydrate; Caustic Potash.

This solution is prepared by dissolving 1 part of the dry sticks in 20 parts water. It is not absolutely essential that this salt be strictly C. P.; there is a good white article ("*rein weiss*") containing a little silica, and perhaps a trace of chlorine, that will answer most purposes, and it is much cheaper than the C. P. article.

The commercial article may contain iron, aluminum, sodium, calcium, organic matter, silica, chlorides, sulphates, carbonates.

44′. **Sodium Hydroxide,** NaOH, is preferred by many chemists to potassium hydroxide, since the former is much cheaper. This solution is made by adding 1 part of the fused substance to 9 parts water. *The impurities* are much the same as in the potassium compound.

40. **Potassium Carbonate,** K_2CO_3; Carbonate of Potassium; Potassic Carbonate; Carbonate of Potash (potassa); *Potassii Carbonas.*

Make this solution by dissolving 1 part of the dry salt, $K_2CO_3 + 3H_2O$, in 10 parts water.

The commercial article may contain iron, aluminum, silica, sodium, chlorides, sulphates, sulphides.

41. **Potassium Iodide,** KI; Iodide of Potassium; Potassic Iodide; *Potassii Iodidum.*

Dissolve 1 part of the salt in 20 parts of water.

The commercial article may contain sodium, iodates, sulphates, chlorides, carbonates.

42. **Potassium Bichromate,** $K_2Cr_2O_7$; Bichromate of Potassium; Potassium Dichromate; Potassic Dichromate; Bichromate of Potash; Red Chromate of Potash; Potassic Acid Chromate; *Potassii Bichromas.*

1 part of the salt is dissolved in 10 parts of water.

The commercial salt may contain iron, calcium, aluminum, sulphates, chlorides.

43. **Potassium Sulpho-Cyanide,** KCyS; Sulpho-Cyanide of Potassium; Potassic Sulpho-Cyanide; Potassium Sulpho-Cyanate.

This solution is made by dissolving 1 part of the salt in 25 parts of water.

The commercial article may contain iron, sulphates, chlorides.

44. **Potassium Ferro-Cyanide,** K_4FeCy_6; Ferro-Cyanide of Potassium; Potassic Ferro-Cyanide; Yellow Prussiate of Potash; *Potassii Ferrocyanidum.*

This solution is made by dissolving 1 part of the crystallized salt, $K_4FeCy_6, 3\,H_2O$, in 12 parts of water.

45. **Disodium Phosphate,** Na_2HPO_4; Sodium Phosphate; Phosphate of Sodium; Disodium-Hydrogen Phosphate; Disodic-Hydric Phosphate; *Sodii Phosphas.*

This solution is prepared by dissolving 1 part of the crystallized salt, $Na_2HPO_4 + H_2O$, in 10 parts of water.

The commercial salt may contain arsenic, iron, lead, sulphates, chlorides.

46. **Barium Chloride,** $BaCl_2$; Chloride of Barium; Baric Chloride; *Barii Chloridum.*

Dissolve 1 part of the crystallized salt, $BaCl_2 + 2H_2O$, in 10 parts of water.

The commercial article may contain calcium, strontium, iron, aluminum, silica.

47. **Calcium Hydroxide,** $Ca(OH)_2$; Calcic Hydrate; Lime Water; *Liquor Calcis.*

This solution is best prepared in the laboratory. "Slake the lime by the gradual addition of 6 parts of water, then add 30 parts of water, and stir occasionally during half an hour. Allow the mixture to settle, decant the liquid and throw this away. Now add to the residue 300 parts of distilled water, stir well, and wait a short time for the coarser particles to subside, and then pour the liquid, holding the undissolved lime in suspension, into a glass-stoppered bottle. When wanted for use, pour off the clear liquid." — U. S. P.

48. Magnesium Sulphate, $MgSO_4$; Sulphate of Magnesium; Magnesic Sulphate; Sulphate of Magnesia; Epsom Salt; *Magnesii Sulphas.*

Dissolve 1 part of the crystallized salt, $MgSO_4 + 7H_2O$, in 10 parts of water.

The commercial salt may contain calcium, iron, silica, zinc, manganese, chlorides.

49. Mercuric Chloride, $HgCl_2$; Bichloride of Mercury; Perchloride of Mercury; Corrosive Sublimate; Corrosive Chloride of Mercury; *Hydrargyri Chloridum Corrosivum.*

Dissolve 1 part of the crystallized salt in 70 parts of water.

The commercial salt may contain iron, lead, calcium, antimony, tin.

50. Silver Nitrate, $AgNO_3$; Nitrate of Silver; Argentic Nitrate; Lunar Caustic; *Argenti Nitras.*

Dissolve 1 part of salt in 70 parts of water.

The commercial salt may contain iron, lead, copper.

51. Lead Acetate, $Pb(C_2H_3O_2)_2$; Acetate of Lead; Plumbic Acetate; Sugar of Lead; *Plumbi Acetas.*

Dissolve 1 part of the crystallized salt, $Pb(C_2H_3O_2)_2 + 3\ H_2O$, in 10 parts of water. If the solution is not clear, filter it.

The commercial salt may contain sodium, calcium, iron, lead, copper, chlorides, nitrates.

52. Ferric Chloride, Fe_2Cl_6; Perchloride of Iron; Sesquichloride of Iron; *Ferri Chloridum.*

Dissolve 1 part of the solid salt, $Fe_2Cl_6 + 6\ H_2O$, in 15 parts of water.

The commercial article may contain ferrous chloride, aluminum, nitrates, sulphates.

53. Alcohol, C_2H_6O; Ethyl Alcohol; Spirits of Wine.

The alcohol used should be the "Spirits of Wine," having a specific gravity of .815, and containing about 95 per cent of the spirit. This should be purchased ready for use.

54. Cobaltous Nitrate, $Co(NO_3)_2$.

This solution is prepared by dissolving 1 part of the crystalline salt, $Co(NO_3)_2 + 5H_2O$, in 20 parts of water.

This solution is used merely for moistening the bead on the platinum wire, and should be kept in a small half-ounce bottle, as this amount will last a long time.

DRY REAGENTS.

55. Ferrous Sulphate, $FeSO_4 + 7H_2O$; Sulphate of Iron; Green Vitriol; *Ferri Sulphas.*

This reagent is used in solution, 1 part of the salt to 10 parts of water; but the solution oxidizes rapidly to a ferric condition, in consequence of which, it is best to make the solution in a test-tube, as required from time to time; the proportions need not be exact.

The dry salt also oxidizes by standing; hence, in practice, a crystal of the salt is dropped into the test-tube, and a little water added; the crystal is now shaken until the white coating of the ferric salt disappears, and the crystal is of a clear green color; this water is now thrown out, and a fresh portion added; heat is then applied to hasten the solution.

56. Sodium Carbonate, Na_2CO_3; Carbonate of Sodium; Sodic Carbonate; *Sodii Carbonas.*

This reagent is used in the form of the dry, powdered salt; the bottle containing it should be kept well corked to prevent the reagent from absorbing the gases of the laboratory.

The commercial salt may contain iron, aluminum, silica, calcium, lead, chlorides, sulphates, sulphides.

57. Sodium Borate, $Na_2O(B_2O_3)_2$; Borate of Sodium; Borax; *Sodii Boras.*

This reagent is used in a dry, powdered form.

The commercial article may contain iron, sodium, aluminum, silica, calcium, chlorides, sulphates.

58. Sodium-Ammonium Phosphate, $NaNH_4HPO_4 . 4H_2O$; Microcosmic Salt; *Sodii et Ammonii Phosphas.*

This is used in a dry state.

59. Ferrous Sulphide, FeS.

The method of using this sulphide is explained in the text, Art. 167.

60. Potassium Chlorate, $KClO_3$; Chlorate of Potassium; Potassic Chlorate; Chlorate of Potash; *Potassii Chloras.*

The crystallized salt is used.

61. Metallic Zinc, Zn.

The granulated metal is employed. This form is obtained by pouring molten zinc into water. It must be absolutely free from arsenic. (See Art. 319.)

REAGENTS FOR THE SIDE-TABLE.

These reagents are those required occasionally by the student. One set should be prepared and placed on a side-table, or in a cupboard conveniently located, so that it is accessible to all the students in the laboratory. The solutions may be kept in 4-oz. bottles similar to those on the student's desk. The corks of all these bottles, excepting those for ether and carbon bisulphide, should be paraffined. The dry salts are to be kept in convenient broad-mouth bottles.

62. Carbon Bisulphide, CS_2; Carbon Disulphide; Bisulphide of Carbon; *Carbonei Bisulphidum.*

This reagent is purchased ready for use. It is very volatile, and the bottle should be closed with a good chemical cork stopper.

63. Ether, $(C_2H_5)_2O$; *Aether;* Sulphuric Ether.

This reagent is purchased ready for use, and the bottle should be closed with a chemical cork stopper.

64. Potassium Sulphate, K_2SO_4; Sulphate of Potassium; Potassic Sulphate; Sulphate of Potash; *Potassii Sulphas.*

Dissolve 1 part of the crystallized salt in 12 parts of water.

65. Potassium Ferri-Cyanide, K_3FeCy_6; Ferricyanide of Potassium; Red Prussiate of Potash.

Dissolve 1 part of the salt in 12 parts of water. This solution will not keep long without undergoing decomposition.

66. Potassium Chromate, K_2CrO_4; Chromate of Potassium; Potassic Chromate.

Dissolve 1 part of the salt in 10 parts of water.

67. Potassium Cyanide, KCy; Cyanide of Potassium; Potassic Cyanide; *Potassii Cyanidum.*

1 part of the solid is dissolved in 4 parts of water. The poisonous nature of this reagent should not be forgotten.

68. Potassium Permanganate, $K_2Mn_2O_8$; Permanganate of Potassium; Permanganate of Potash; *Potassii Permanganas.*

Dissolve 1 part of the crystallized salt in about 500 parts of water.

69. Sodium Sulphite, Na_2SO_3; Sulphite of Sodium; Sodic Sulphite; *Sodii Sulphis.*

Dissolve 1 part of the crystallized salt, $Na_2SO_3 + 7\,H_2O$, in 5 parts of water.

70. Calcium Sulphate, $CaSO_4$; Sulphate of Calcium; Calcic Sulphate; *Calcii Sulphas.*

This solution is made by dissolving all the salt, $CaSO_4 + 2H_2O$, that the water will take up; or, in other words, it is a saturated solution.

71. Calcium Chloride, $CaCl_2$; Chloride of Calcium; Calcic Chloride; *Calcii Chloridum.*

Dissolve 1 part of the salt, $CaCl_2 + 6H_2O$, in 8 parts of water.

72. Stannous Chloride, $SnCl_2$; Protochloride of Tin.

To 6 parts of water add 1 part of the crystallized salt, $SnCl_2 + 2H_2O$; then add hydrochloric acid, drop by drop, until the solution turns clear.

73. Copper Sulphate, $CuSO_4$; Sulphate of Copper; Cupric Sulphate; Blue Vitriol; Blue Stone; *Cupri Sulphas.*

Dissolve 1 part of the crystallized salt, $CuSO_4 + 5H_2O$, in 8 parts of water.

74. Starch Paste. This solution is made by dissolving 1 part of starch in 500 parts of water. In case the student desires a solution of starch paste and potassium iodide, he may place a little of the starch paste solution in a test-tube, and add a drop or two of the reagent potassium iodide solution.

75. Ammonium Molybdate, $(NH_4)_2Mo_4$. Dissolve 60^g of the dry salt in 400^{cc} of reagent ammonia solution; add 400^{cc} of distilled water; then cautiously add 500^{cc} nitric acid (sp. grav. 1.4).

GRADUATED SOLUTIONS, Etc.

76. Clark's Soap Solution is prepared by dissolving 10^g of good castile soap in 1^l of dilute alcohol containing about 35 per cent of the spirit. The dilute alcohol may be prepared from the reagent alcohol by mixing 368.5^{cc} alcohol with 631.5^{cc} distilled water.

To test the soap solution a reagent solution of calcium chloride is required. This solution is prepared by dissolving 1^g of Iceland spar in hydrochloric acid; the solution is then evaporated to dryness to expel any excess of acid, after which the residue is dissolved in 1^l of distilled water. Now if 12^{cc} of the solution just formed be diluted to 70^{cc} and brought into a flask, it will require just 13^{cc} of the soap solution to make a permanent lather, provided the soap solution be of the right strength. In case the soap solution is not of the right strength, it must be made so, or allowances must be made when calculating the degrees of hardness of a sample of water.

The soap solution deteriorates by standing.

77. Nessler's Solution is prepared by dissolving 13^g mercuric chloride, $HgCl_2$, in about 400^{cc} of distilled water; now 35^g of potassium iodide, KI, are dissolved in (say) 200^{cc} of water, and these two solutions are then mixed. To this solution add 100^g of solid potassium hydroxide, KOH, and when it is dissolved and the solution cool, dilute the whole with water to 1^l. Keep this solution in a dark, cool place, and take a portion of it in a small bottle for immediate use.

Before using the solution it is necessary to "sensitize" it; this is accomplished by adding slowly a saturated solution of mercuric chloride, with constant stirring, until the red precipitate first formed ceases to dissolve. Either filter the solution or allow it to stand till the solids have all subsided. It is now ready for use, and should be of a light, straw-yellow color. This solution loses its sensitiveness by standing.

78. A Few Graduated Solutions have been mentioned in the text; as, for example, Barium Hydroxide Solution and Oxalic Acid Solution, p. 148; Silver Nitrate Solution, p. 107; Iodine Solution, p. 181; Ammonium Chloride Solution, p. 72. These have been sufficiently described, so that there is nothing to add, unless it be to note that in case these solutions prove too strong that they may be diluted to some other standard of strength; for example, it is evident that if 1^{cc} of the ammonium chloride solution be added to 99^{cc} of distilled water, 1^{cc} of the solution thus formed will correspond to $.01^{mg}$ of ammonia. It is usually necessary to work, when estimating the ammonia of drinking-water, with this dilute solution. Now, if the burette used be graduated to $.1^{cc}$, it is evident that by this means the ammonia in drinking-water, etc., may be determined to $.001^{mg}$. It might be well, in this connection, to call attention to the extreme accuracy obtainable in titration.

N.B. A few words of caution concerning the estimation of chlorine may be in place here. It is evident the chromate used for an indicator must be free from chlorine; also, in order to have the end reaction sharp, the solution must be exactly neutral.

In estimating ammonia, the water used in connection with the standard solution of NH_4Cl must be free from ammonia. This may be obtained by taking (say) 2^l of distilled water, and distilling until the distillate gives no reaction for ammonia. The water remaining in the retort is evidently free from ammonia.

INDICATORS.

Solutions of various substances are employed to indicate what is called "End Reactions." The method of using these indicators has been explained in the text. It now remains to show how a few of these solutions are made.

79. Litmus Solution is prepared by digesting for several hours 10^g of solid litmus with 500^{cc} of distilled water; allow the liquid to become clear, or filter it when it is ready for use, when the end reaction is to be acid; one portion of it may be prepared for solutions, when the end reaction is to be alkaline, by adding to it a few drops of acetic acid.

80. Cochineal Solution is obtained by digesting 3^g of the powder in 250^{cc} of 20 per cent alcohol. This is very sensitive; acids bleach it, alkalies redden the bleached solution.

81. Phenol-Phthalein Solution is made by dissolving 1 part of the solid in 100 parts of 60 per cent alcohol; this gives a colorless solution which is reddened by alkalies. This red solution is bleached by acids. It may be used as a *qualitative test* for carbon dioxide. See "American Chemical Journal," 3, 55, 232. For a paper on Lakmoid, Phenol-Phthalein, and other indicators, see "The Chemical News" of July 10, 1885, p. 18, and July 17, 1885, p. 29.

82. A Soap-Bubble Solution is prepared thus: To about 100^g of finely-cut best castile soap in a litre flask add nearly a litre of distilled water; shake until the solution is saturated with soap; then allow it to settle clear; to two volumes of soap solution add one volume of glycerine.

GENERAL NOTE. In order to lessen the first cost of equipping the laboratory, many of the reagents, enumerated as belonging to the student's desk, may be placed on the side-table. Many good laboratories are thus arranged.

WORKING MATERIAL.

The substances enumerated under this heading are arranged in the same order as the Elements and their compounds in the text, and none are repeated. It is not necessary in every case that the chemicals which follow should be chemically pure. The reagents, etc., already named are not given.

83. Introduction. Galena; iron filings; flowers of sulphur.

84. Oxygen. Mercuric oxide; red lead; manganese dioxide (C. P.); bark charcoal; iron wire; broken watch-springs; phosphorus; zinc foil; pyrogallic acid.

85. Hydrogen. Metallic sodium and potassium; mercury; well-water barium dioxide.

NOTE. For generating large quantities of hydrogen when purity is not especially requisite, sheet zinc may be employed; this is cut into bits, and to help the action along a few nails may be thrown into the generator.

86. **Nitrogen.** Quicklime; ammonium chloride; ammonium nitrate (C. P.); copper filings; potassium nitrate; spirits of turpentine.

87. **Chlorine.** Indigo solution; sodium chloride.

88. **Bromine.** Potassium bromide; bromine.

89. **Iodine.** Iodine.

90. **Fluorine.** Calcium fluoride; beeswax, or paraffin.

91. **Carbon.** Lampblack; graphite; various kinds of coal; boneblack; sugar; sodium acetate; yeast; calcium carbonate; magnesium ribbon; clam shells, snail shells, corals, and other carbonates.

92. **Sulphur.** Roll sulphur; iron pyrites.

93. **Silicon.** As many varieties of silicon dioxide as possible.

94. **Boron.** Boric acid.

95. **Phosphorus.** Stick phosphorus; red phosphorus.

When working with the metals, it is desirable to have as many ores of each metal as possible; not that these ores are absolutely indispensable to the work in the text, but because of the advantage the student may derive from their examination or from working with them.

96. The **First Group Metals.** Metallic silver and ores of silver; metallic mercury and ores of mercury; metallic lead in its commercial forms, and ores of lead.

97. **Second Group Metals.** Arsenic and arsenic trioxide; antimony, antimony sulphide, and ores of antimony; metallic tin in its commercial forms, and ores of tin; metallic bismuth and ores of bismuth; sheet copper, native copper, and ores of copper; metallic cadmium, ores of cadmium.

98. The **Third Group Metals.** Iron in its commercial form and ores of iron; chrome alum or other chromium salts; metallic aluminum and as many commonly occurring aluminum compounds as possible; metallic nickel and ores of nickel; cobalt ores; manganese ores; commercial forms of metallic zinc.

99. The **Fourth Group Metals.** Barium dioxide, hydroxide, and as many barium-bearing minerals as possible; strontium nitrate; many calcium bearing minerals; metallic magnesium ribbon, and many magnesium-bearing minerals.

The **Fifth Group Metals** are already provided for.

GENERAL APPARATUS.

Under this heading is included that apparatus which is of general utility. The teacher may need some of it for special purposes, while some of it is so placed that the students may have access to it at any time. Much of this apparatus may be used in physics also.

100. A Becker or **Troemner Balance**, Fig. 23, is to be recommended on account of its cheapness, neatness, accuracy (sensitive to 2^{mg}), and durability. By placing a small shelf or table over one pan, so that the balance may play freely, it will answer well for specific gravity. The author's students have used this balance for three years, and it is still as good as new. Accompanying it is a set of weights in a polished, velvet-lined box, with forceps, and a tray divided into compartments for the small weights, and covered with a glass slide. These weights were imported at a cost of \$3.50; they run from 50^g to 1^g in brass and 500^{mgs} to 1^{mg} in platinum.

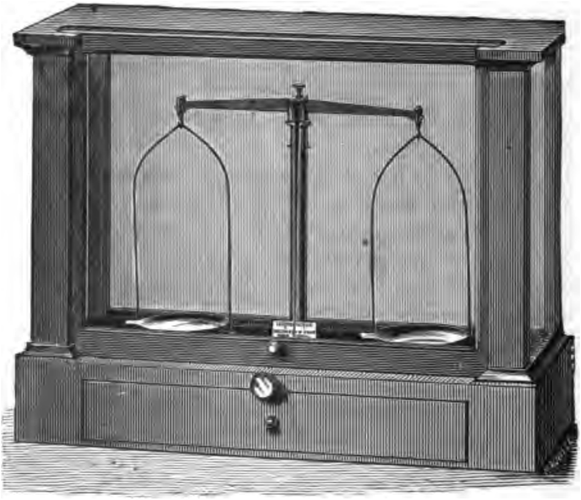

FIG. 23.

101. A Pair of Counter-Poised Watch-Crystals are useful in weighing those substances which would attack the pans of the balance.

102. A Weighing Flask for iodine and other volatile substances is desirable.

103. A Specific Gravity Bottle of 50^{cc} capacity is useful in determining the specific gravity of fluids.

104. A Pair of Hydrometers. One for fluids lighter than water, and one for fluids heavier than water.

105. A Pair of Good Centigrade Chemical Thermometers. One graduated from $-20°$ to $+240°$, and one from $-10°$ to $+360°$.

106. Graduated Flasks. One 1^{l}, one $\frac{1}{2}^{l}$, and one $\frac{1}{4}^{l}$.

These are fitted with glass stoppers, and bear only one mark around the neck. These are useful when 1^{l}, etc., is wanted quickly.

107. Litre Cylinder for mixing reagent solutions. These are graduated into cc's to read up and down.

108. Two Burettes, capacity 50^{cc} each; graduated to 0.1^{cc}. These are used in titration.

109. A Pipette, capacity 5^{cc}, graduated to 0.1^{cc}. Used for taking out small quantities of liquids from bottles, etc.

110. A Lipped Graduated Jar, capacity 100^{cc}, graduated to 1^{cc}. Used in measuring out liquids.

111. Ure's Eudiometer. This is shown and explained in Fig. 7.

112. Hofmann's Apparatus, as shown and explained in Fig. 3.

113. Spectroscope. Spectroscopes are now to be had quite reasonably. The needs of the school should determine the expense of the instrument purchased.

114. Bell Jars are used in experimenting with gases. Those used in connection with the air-pump may be employed, or large bottles may be cut off at the bottom. This may be accomplished by cutting a crease around the bottle with a three-cornered file; this crease is then followed up with a minute blow-pipe flame until the bottom cracks off. The edges may then be ground smooth on a sheet of emery-paper stretched on a flat board.

115. Large Beakers, Funnels, Evaporating Dishes, and Ring Stands similar to those shown in the Frontispiece, only larger, are found useful in preparing solutions, reagents, etc.

116. Retorts and Receivers, similar to those shown in Fig. 14, are used in distillation, etc.

117. **A Liebig's Condenser** is often used in connection with the retorts.

118. **Tall Jars** are useful in experimenting with gases.

119. **An Iron Mortar** and a **Porcelain** or a **Wedgewood-Ware Mortar**, with pestles.

120. **Assorted Glass Tubing** of various sizes suitable for "hydrogen tones," connections, etc.

121. **Funnel Tubes for Generators**, as shown in Fig. 5.

122. **Blast-Lamp**, for alcohol or gas, is useful in working glass.

123. **A Copper Oxygen Retort**, for generating oxygen. An iron retort may be used, or a common glass generating flask will serve the same purpose.

124. **Mercury Trough of Porcelain.**

125. **A Hydrogen Pistol** may be made from a gas-pipe 1½ in. in diameter, and 6 in. long. One end is closed with a cap; a small opening is drilled in for a vent, and the mouth is closed with a common cork.

126. **A Pneumatic Trough.** There are many designs in use. As a general rule, the simpler the trough, the better.

127. **Gas Holders.** Any tinsmith can make very satisfactory gas holders. Or they can be made from a barrel, and a cask that will go inside the barrel. The heads are removed; the barrel is filled with water, and the cask is inserted in the barrel and suitably weighted; a stop-cock, for attaching rubber-hose, is inserted in the head of the cask.

128. **Chemical Corks** and **Rubber Stoppers** of assorted sizes.

129. **Rubber Tubing** of assorted sizes, for connections, etc.

130. **Rubber Gas-Bags.** One of 2 gals., and one of 1 gal. capacity.

131. **Oxyhydrogen Blow-Pipe.** One form of this apparatus is shown in Fig. 8. Prof. Weitbrecht has constructed a cheap instrument from ⅛-in. gas fixtures. The instrument is T shaped; into the stem of the T is screwed a Springfield musket cap-nipple which serves as a jet; in each arm of the T is a stop-cock. The hydrogen is admitted into one arm and the oxygen into the other. Illuminating gas may be used in place of hydrogen.

132. **A Furnace**, known as the Fletcher Furnace, and provided with bellows and a blast-jet for illuminating gas, is not expensive, and will fuse such metals as gold, silver, etc.

133. Crucibles. Hessian crucibles and plumbago crucibles are used. The sand, or Hessian crucible, is inexpensive, and may be bought in nests.

THE LIBRARY.

A reference library should be kept in the laboratory. It should be easy of access, and the students should be permitted to make use of any book at any time. Books should not be taken out of the laboratory. In the following list no attempt at completeness is made; a few good books that are within the reach of all schools are named. Roscoe and Schorlemmer's "General Treatise" will be found useful for general descriptive work.

Douglas and Prescott's "Qualitative Analysis," or a standard edition of Fresenius's "Qualitative Analysis," will be useful in qualitative work.

Sutton's "Volumetric Analysis" is recommended for methods of titration.

Fresenius's "Quantitative Analysis" is useful, if quantitative work is attempted.

Elderhorst's "Blow-Pipe Analysis" is to be used in expanding any work with the blow-pipe.

Wanklyn's "Analysis of Water, Milk, and Air," may be used in case it is desired to do work in that direction. These books are published in separate volumes.

Dana's "Mineralogy" is valuable as affording information concerning ores, coal, etc.

Gore's "Electro-Metallurgy" will afford information in that direction.

Some good work on Spectrum Analysis is desirable. Schellen, though popularly written, is good. Roscoe's work is more technical.

The "U. S. Dispensatory," and the "Pharmacopœia" are often useful. Bailey's "Chemist's Pocket-Book" contains many valuable data for computations, conversions, etc., etc.

One or two chemical journals, as "The Chemical News" and the "American Journal of Chemistry," will serve to create an interest, by calling the student's attention to the present tendencies of the science.

In response to numerous inquiries from teachers, concerning apparatus, etc., the author would take this occasion to say that he will gladly give any information in his power concerning the same; and, in case any school wishes aid in purchasing, that he has made arrangements with Messrs. Eberbach and Son, Ann Arbor, Mich., whereby any apparatus or chemicals necessary for this text can be supplied promptly, and at the lowest market price for the high grade of goods recommended. All correspondence on this subject should be addressed to the author. A priced list will be sent on application.

Data for Converting Metric and English Weights and Measures.

1^{mm} = 0.0394 in.
1^{cm} = 0.3937 in.
1 in = 2.539954^{cm}.
1 cu. in. = 16.386176^{cc}.
1^{cc} = 0.06103 cu. in.
1^{l} = 61.02709 cu. in.

1^{g} = 15.43235 grains.
1 grain = 0.0648^{g}.
1 lb. avoirdupois = 453.59^{g}.
1 oz. avoirdupois = 28.349954^{g}.
1 gal. U. S. = 231. cu. in.
1 gal. Imp. = 277¼ cu. in.

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